Gasoline and the Gasoline Engine.

By O. Thornycroft and A. Ferguson.

Consumption.

Up to the end of 1930, despite the trade depression which had existed then for at least a year, the consumption of gasoline continued to increase. The rate of increase had, however, rapidly diminished since 1925. This is shown by the upper curve in Fig. 1, in which is plotted the annual percentage increase in the total consumption of gasoline within the U.S.A. The lower curve shows the diminishing rate of increase in the number of motor vehicles registered in that country.

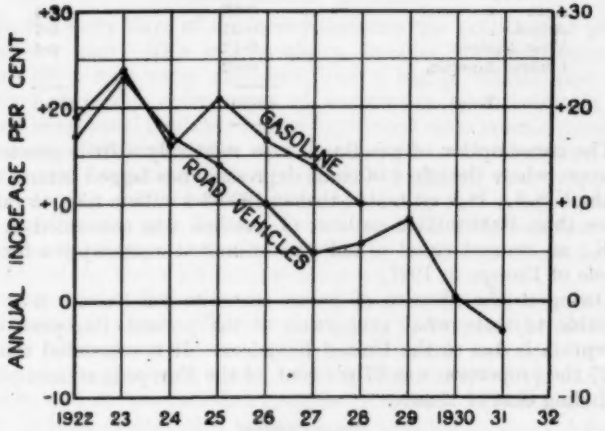

Fig. 1.

From 1925 to 1928 the percentage increase in the total consumption of gasoline in the U.S.A. had been greater than the increase in the number of road vehicles registered. This was due partly to the growth of aviation during that period. No completely reliable figures have been obtained for the total consumption of gasoline since the end of 1928, and the upper curve in Fig. 1 has therefore not been extended beyond that date. From the trend shown by the consumption curve to follow that of the vehicles, albeit with a possible lag, it seems probable that the rate of increase in gasoline consumption fell to zero towards the end of 1931.

In the United Kingdom the fall in annual increase has been less rapid, and has been relatively delayed. Between the years 1929 and 1930, the increase in the U.K. was still as high as 20 per cent. Over the same period in the U.S.A. the increase was only 0·5 per cent. In 1927, it is estimated the world consumption of gasoline was 45 million tons. Of this, 34 million tons, or 76 per cent., was consumed in U.S.A. Taking the year 1927, for which year careful estimates of consumption were prepared by the American Bureau of Foreign and Domestic Commerce, we find that the world consumption of gasoline was distributed as is shown in Table 1.

TABLE I.

	Tons (mill.).	Percentage of world consumption.
North America	36·0	79·5
Europe	6·7	14·8
Australasia	0·73	1·6
South America	0·71	1·6
Asia	0·63	1·4
Africa	0·34	0·7
West Indies	0·17	0·4
Central America	0·02	—
Total	45·30	100·0

The consumption of gasoline is now relatively a little greater in Europe, where the effect of trade depression has lagged behind that of the U.S.A. It is estimated that in 1930 3·4 million tons, or rather more than 1000 million gallons, of gasoline was consumed in the U.K., an amount equal to half the estimated consumption for the whole of Europe in 1927.

Owing to the absence of recent statistics for Russia, it is not possible to state what proportion of the present European consumption is due to the United Kingdom. It is estimated that in 1927 the proportion was 37 per cent. of the European consumption, including that of Russia.

PRODUCTION.

The production of gasoline has, in recent years, exceeded the demand, with the result that prices in many important areas have fallen below costs. Fortunately there are signs that this state of affairs will be remedied in time, but the present great number of separately owned oil-producing concerns in the U.S.A. makes co-operation very difficult. The production in that country is so much greater than in any other area that the conditions in the U.S.A. will necessarily continue to dominate the market prices of the world. Both in 1927 and in 1928 the quantity of crude oil produced in the U.S.A. represented practically 70 per cent. of the world production. Due to the relatively great importance of the

motor industry in the U.S.A., the process of cracking heavy oils to produce gasoline has been used to a greater extent than elsewhere. This has resulted in a production of gasoline in the U.S.A. which is greater, relatively to world production, even than is shown by figures for the production of crude oil. It is not possible to state the present world production of gasoline, but in 1929 it was almost certainly between 55 and 60 million tons. Of this production the 51 million tons produced in the U.S.A. was composed as follows :—

Straight-run	56 per cent.
Cracked	33 „
"Casinghead gasoline"	11 „

In addition there was produced a quantity of benzole amounting to 0·7 per cent. of the gasoline production.

Anti-Knock Quality.

In the early days of the motor industry the volatility of petrol was very high. This was necessary, because the carburettors of those days were most imperfect, and a highly volatile fuel was needed to enable some types of carburettor to function at all. There is a general tendency for the lighter and more volatile paraffins to possess relatively high anti-knock values; furthermore, the compression ratios employed in the early engines were relatively low. It was not therefore until the rapidly increasing demand for gasoline brought heavier, low anti-knock, fractions into use that the significance of detonation and the advantage of anti-knock quality in the fuel were fully appreciated.

Immediately after the war, scientific research was commenced on gasoline as a fuel. The purpose was to investigate the influence of the different constituents of gasoline on the functions of the engine. A scale of anti-knock values in terms of two fuels, namely, toluene and an aromatic-free gasoline, was used. By experiments in a variable compression engine it was possible to give "toluene values" to some of the pure hydrocarbons of which gasolines are composed.

The toluene value scale could be expressed in terms of compression-ratio in the variable compression engine used for the tests. The compression ratio scale of "H.U.C.R." or "highest useful compression ratio" was found to be more convenient for determining the composition of a blend to give a certain anti-knock quality to a motor-spirit. The H.U.C.R. scale, therefore, instead of the toluene value, came into more general use. The newer "octane number" scale recently adopted by the American Co-operative Fuel Research Committee has received acceptance in Great Britain, and is likely to be adopted in all countries. The

scale is based on the anti-knock characteristics of *iso*-octane and *n*-heptane when mixtures of these substances are made to match in detonation the samples of gasoline under test. The tests also have to be made in a certain type of engine under very exactly controlled conditions of temperature and method of operation.

The anti-knock characteristics of some typical hydrocarbons are shown in Table II. The values are expressed in H.U.C.R. of the Ricardo E.35 type engine fitted with the five-valve head, with

TABLE II.

Fuel.	Boiling pt. °C.	Effective calorific value B.Th.U. per Imp. gall.	H.U.C.R. in E.35 engine.
Paraffins—			
Propane	—38	110,500	>8
i-butane	+ 1	119,000	7·5
n-pentane	36	123,500	6
n-hexane	69	134,000	5
n-heptane	98	135,000	3·7
Naphthenes—			
Cyclohexane	81	149,000	>6
Methylcyclohexane	96	147,000	6
Aromatics—			
Benzene	80	154,200	>8
Toluene	110	153,600	>benzene
p-xylene	138	154,000	>toluene
Gasolines (*U.K.*) (*marketed* 1931)—			
No. 1 motor spirits	35/200	141,000 approx.	5·55 av. value
Commercial spirits	40/200	142,000 „	5·35 „
Aviation (coml.)	50/170	140,000 „	5·7 „

NOTE.—The H.U.C.R. values (except for the gasolines and for heptane) are approximate only, since they were determined from engine tests made on somewhat impure substances.

water-cooling at 60° C. and with air heating of 1350 watts. The curves in Fig. 2 show respectively the H.U.C.R. of mixtures of pure benzene and *n*-heptane and of mixtures of *iso*-octane and *n*-heptane. The latter curve represents the approximate relation between H.U.C.R. in the E.35 engine and octane number in the C.F.R. engine.

Pure Hydrocarbons.—In Fig. 3 and in Table III. results are given of a number of more recent tests carried out by R. Stansfield and his assistants at the laboratory of the Anglo-Persian Oil Co. The hydrocarbons were prepared by Dr. S. F. Birch. The engine used for the tests was the Ricardo E.5 type variable compression engine. The curves in Fig. 3 illustrate, according to the extent of their upward tendencies, the relative anti-knock characteristics of the hydrocarbons named. Toluene, benzene and cyclohexane all exhibit continuously upward curves; but the unsaturated compound cyclohexene shows a curiously varying effect on detonation, depending upon its degree of concentration in the gasoline. It is

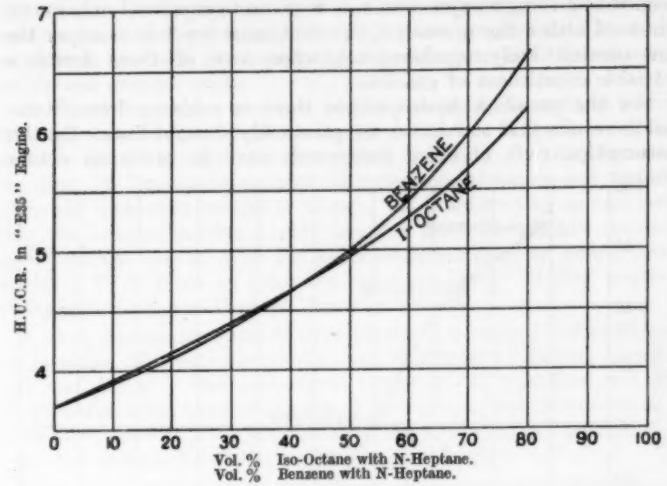
7
6
5
4
H.U.C.R. in "E35" Engine.
BENZENE
I-OCTANE
0
10
20
30
40
50
60
70
80
90
100
Vol. % Iso-Octane with N-Heptane.
Vol. % Benzene with N-Heptane.

FIG. 2.

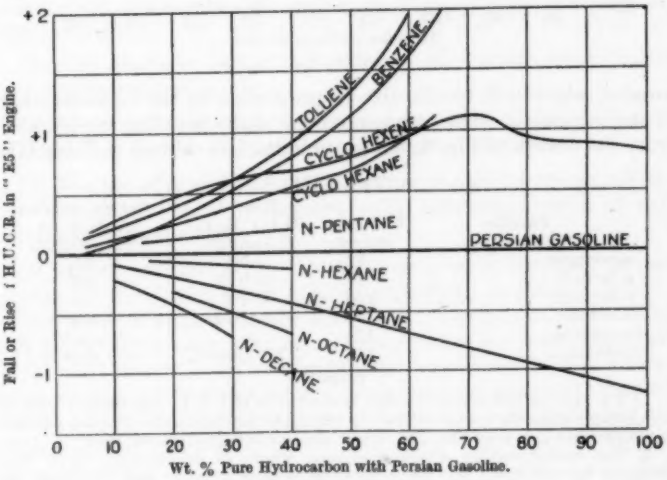
+2
+1
0
-1
Fall or Rise { H.U.C.R. in "E5" Engine.
TOLUENE
BENZENE
CYCLO HEXENE
CYCLO HEXANE
N-PENTANE
PERSIAN GASOLINE
N-HEXANE
N-HEPTANE
N-OCTANE
N-DECANE
0
10
20
30
40
50
60
70
80
90
100
Wt. % Pure Hydrocarbon with Persian Gasoline.

FIG. 3.

seen that no single expression can be given to represent anti-knock value of either the aromatics, the naphthene (cyclohexane), or the unsaturated body (cyclohexene), when any of these forms a variable constituent of gasoline.

For the paraffinic hydrocarbons there is evidence from Stansfield's results that the curves are practically straight lines. On this assumption each of these compounds may be given an octane

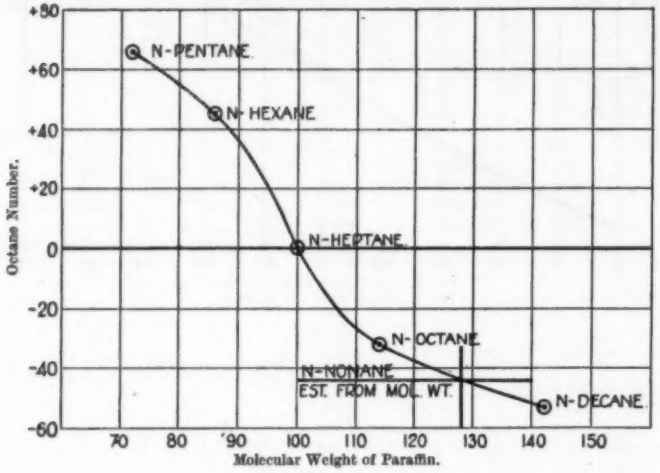

FIG. 4.

number which will be effective in proportion to the concentration of the substance. The octane numbers of the paraffins, as deduced from the curves of Fig. 3, are given in the last column of Table III.

TABLE III.

Paraffin hydrocarbon.	Molecular weight.	Rise of H.U.C.R. in E.5 engine.	Octane number (calc. from E.5 results).
n-pentane	72	+0·4	66
n-hexane	86	—0·35	45
n-heptane	100	—1·2	0
n-octane	114	—1·75	—32
n-nonane	128	—	—44 see Fig. 4
n-decane	142	—2·3 approx.	—53 approx.

NOTES.

1. The rise (or fall where the sign is minus) in H.U.C.R. has been arrived at by extrapolating the curves (shown in Fig. 3) to 100 per cent. For the paraffin hydrocarbons it is seen that the curves are practically straight lines.

2. The corresponding octane numbers, where of minus sign, have been deduced by reversing the curve relating octane number and H.U.C.R. for the E.5 engine.

For the heavier bodies negative octane numbers have had to be used, since their " pro-knock " tendencies are greater than that of *n*-heptane, of which the knock characteristic provides the zero for the octane number scale.

In Fig. 4 the octane numbers of the paraffin hydrocarbons have been plotted against their molecular weights. When a smooth curve is drawn through the five points obtained, an estimate can be given of the octane number of n-nonane, although not tested since the molecular weight is known. It is interesting to observe that the octane number (—44) deduced from Stansfield's results agrees almost exactly with the value obtained from an actual test made by T. A. Boyd on n-nonane using the Delco " S. 30 " engine at the laboratories of General Motors in Detroit.

A most systematic series of experiments was carried out at these laboratories, of which the results were published by Lovell, Campbell and Boyd[1]. The anti-knock values of 27 paraffins and of 25 aliphatic olefines were determined, and several important conclusions were shown. For the paraffins the following generalisations were demonstrated and the quantities were found :—

(1) In any homologous series the anti-knock value diminishes with the increasing length of the chain of carbon atoms.

(2) The introduction of methyl groups into a carbon chain of given length always increases the anti-knock value of the resulting paraffin and the increase for each methyl group added is substantially constant.

For the aliphatic olefins the following conclusions were drawn and values were given :—

(1) The anti-knock value of a straight chain olefin is always greater than that of the corresponding normal paraffin.

(2) For the aliphatic olefins, as was found also for the paraffins, the anti-knock value diminishes with increasing length of the saturated carbon chain.

(3) In any isomeric series the anti-knock value increases as the position of the double bond is more centralised in the molecule.

The research work using the Ricardo E. 35 engine in 1919—1920 had almost immediate economic results. Gasolines from a number of different sources could now be blended, in commercial quantities, to produce a motor fuel having a predetermined standard of anti-knock. The results of the engine experiments were published in 1921, and since that date there has been a steady rise in the

[1] Lovell, Campbell and Boyd, *Ind. Eng. Chem.*, 1931, **23**, 26.

anti-knock quality of motor fuels. In Table IV are shown the improvements made in the average anti-knock quality of the chief petrols marketed in the United Kingdom during the last ten years.

TABLE IV.

Year of average sample (United Kingdom).	No. 1 grade gasoline. Octane number (in C.F.R. eng. approx.).	Commercial grade gasoline* Octane number (in C.F.R. eng. approx.).
1922 ..	51 ..	43
1925 ..	55 ..	53
1928 ..	58 ..	55
1931 ..	68 ..	61

NOTE.—The gasoline generally available to the public in England just after the Great War had an octane number of about 35.

The octane numbers given in the table, except those for the year 1931, are necessarily only approximate. The earlier values have been deduced from H.U.C.R. determinations in the E. 35 engine, and there is no accurate relation between the anti-knock values in one engine and those obtained in another. This is due to the differing reactions of various hydrocarbons to detonation in different engines. The octane numbers, except the latest given in the table, may be in error as much as 5 numbers in absolute value, but consecutive values are likely to be correct relatively to within ±2.

Lead Tetra-ethyl.—In the U.S.A. the demand for "premium" priced motor fuels having high anti-knock value has steadily grown. This is shown by the increasing quantity of "ethyl gasoline" sold in that country. The quantities, in Imperial gallons, have been reported as follows :—

Year of consumption.	Ethyl gasoline sold in U.S.A.
1929	1035 million gallons
1930	1545 „ „
1931	1830 „ „

In view of the falling increases in the total annual consumptions of gasoline, the rapidly increasing sales of "leaded" fuels is most remarkable. The last year's sales in the U.S.A. probably represents nearly 13 per cent. of the total quantity of gasoline used in that country in the same year. In the United Kingdom also the use of lead tetra ethyl has greatly increased, but, so far, to a less striking degree.

Casinghead Spirit.—The use of "casinghead gasoline" obtained by the scrubbing of gas from petroleum wells, has been much increased since the year 1927. This has led to a general improvement in the anti-knock values of motor spirits on account of the high resistance to detonation shown by paraffins such as pentane, butane, etc. The propane is mostly removed. Owing, however,

to the danger of vapour-locks being formed in the fuel-pipe or carburettor, it has been found necessary to limit the vapour pressure or alternatively the lowness of the temperature at which 10 per cent. is distilled, and this has imposed a limit to the proportion of high anti-knock paraffins that can be used.

Benzole.—By blending coal-produced benzole with gasoline is that deficient in anti-knock properties, an excellent motor spirit may result. The effect of the benzole must always be to raise the octane number and to increase the calorific value per unit of volume. Per unit of weight the calorific value must necessarily be reduced by the addition of benzole. For road vehicle and stationary engines the advantage in adding benzole in relatively high concentration is unquestionable, but for aircraft, on account of the higher cycle-temperatures involved, it may be doubtful. There are economic questions relating to supply that limit the use of benzole in motor fuels.

Alcohol.—Both ethyl and methyl alcohols possess anti-knock qualities even higher than that of benzole. The calorific values of these alcohols, on the other hand, are relatively very low. The following table illustrates their position as fuels :—

Fuel.	Effective calorific value. B.Th.U./gal.	B.Th.U./lb.
Petroleum gasoline (av.)	140,000	19,000
Benzole (coal dist.)	152,000	17,500
Ethyl alcohol 98·5 per cent. ..	94,500	11,840
Methyl alcohol 100 per cent. ..	85,200	10,690

If equality in price between alcohol and light petroleum, either in terms of volume or of weight, be assumed, it can be shown that there may be a technical advantage (higher volume efficiency and lower cycle temperature) in the use of ethyl or methyl alcohol as a constituent of motor fuel. The further assumption must be made that the available light petroleum to be used in the blend is deficient in anti-knock qualities and is therefore unable by itself to command the market price of motor spirit. A technical difficulty exists in ensuring that the alcohol remains in true solution in a blend with petroleum under ordinary conditions of storage and service, owing to the possible accidental addition of water. In view of the greatness of the sources and cheapness of supply of petroleum spirit, and with the existing means of maintaining and even raising the anti-knock properties of gasoline, the general use of alcohol as a motor fuel is likely to be long delayed.

Aircraft Fuels.—The progressive improvement in the anti-knock quality of gasolines used for aircraft can be less definitely shown. Many privately owned aeroplanes and some public passenger

machines have been fuelled with "No. 1 grade gasoline." Reasons of price economy and the greater availability of motor spirit, as compared with so-called "aviation" fuel, have brought this about. Technically, the need for high anti-knock quality in gasoline for aircraft is greater than it is for motor fuels. The average "load factor" of an aeroplane engine is much higher, and the economic necessity for high compression (with its consequent high fuel efficiency and power) is greater for aircraft than it is for road vehicles. This has been fully realised by those responsible for the development of war machines and, more recently, by those in charge of air-passenger services. The supercharging of aircraft engines has lately become more general, and the effect of supercharging on detonation in an engine is similar to that of raising its compression.

As a result of these factors which influence fuel quality, two standards of anti-knock value are demanded for aircraft fuels. The first standard, with an octane number of about 68, is for use in engines which, on occasions, may be run on motor spirit. The second standard is very much higher and requires an octane number of at least 76. In anti-knock value, such a fuel complies with the British Air Ministry specification D.T.D. 134.

Engine Carbonisation and "Ring-Gumming."

The importance of avoiding detonation in air-cooled engines has been greatly emphasised by the recent discovery that "ring gumming," which is the sticking of piston-rings in their grooves, may be brought about by even slight detonation. For many years it has been known that free carbon is produced under conditions of detonation in an engine, even though the fuel-air ratio may be lower than that giving maximum power. It was known that carbon so produced was ejected as soot in the exhaust gases; but it now appears that under detonating conditions some of the carbon may remain behind in the engine, and so clog the action of the piston-rings. If this occurs, the piston is generally overheated by the leakage of hot gases past the rings, and "burning" of the piston often follows.

In road vehicle engines, with their lower temperature conditions, "ring gumming" seldom occurs. It is not yet known whether detonation promotes the rate at which carbon deposits are formed under the cooler conditions of water-cooled engines.

Volatility of Fuel.

There are no sharply defined limits in the engine requirements of fuel volatility. The requirements, which are those of both automobile and of aircraft engines, are briefly these: Easy starting from cold; rapid acceleration; little condensation of fuel and oil dilution; freedom from gaslocks in the fuel system.

Engine experiments appear to show that fuel volatility, so far as it affects engine acceleration and fuel condensation, is measured by the lowness of the "dew-point." It is also sufficiently well indicated by the lowness of the 70 per cent. temperature in the A.S.T.M. distillation test. The latter temperature is given below for typical gasolines at present marketed in the United Kingdom :—

Fuel.	70% temperature ° C. (A.S.T.M.).
No. 1 grade motor spirit	137
Commercial grade spirit	144
Aviation (commercial)	112

For starting with a cold engine, it is necessary to increase the ratio of fuel to air beyond that required for combustion under running conditions. The reason for this is that when the cylinder is cold only part of the fuel is evaporated, and enough additional fuel must be supplied in order to provide a combustible mixture from the vapour of the lighter fractions only. No exact measure of fuel volatility can be given for such conditions which depend on the mechanical means available for enriching the mixture; but the lowness of the 20 per cent. temperature (in the A.S.T.M. distillation) may be taken as a guide for "startability."

As a measure of "gassing" tendency the vapour pressure of the fuel at 0° C. may be found to be sufficiently accurate. More scientifically, the vapour pressure may be measured at a temperature approximating to the temperature likely to be met with in service, and a limit has to be set which will provide against vapour lock under the worst known conditions of operation. The British Air Ministry provides against gassing by specifying a maximum proportion of 5 per cent. to distil from the fuel below 50° C.

The correlation of fuel volatility and engine performance has been very ably examined by G. G. Brown.[2] The conditions leading to gassing and vapour-lock have been analysed by Dr. O.C. Bridgeman.[3] of the American Bureau of Standards. The lowness of the 10 per cent. temperature (in the A.S.T.M. distillation) is shown to give a truer measure of gassing tendency than can be gained by a vapour pressure test.

Purity of Fuel.—Solid impurities, undissolved water, and mineral acid may be assumed to be absent. Such bodies are easily detected and are readily removed. Small quantities of gummy materials are soluble in gasoline but in storage and in use they may separate. The increased use of cracked spirit has brought attention to this

[2] G. G. Brown, Dept. Eng. Res. Mich. Univ., Bull. 14, 1930.

[3] Articles of O. C. Bridgeman, E. W. Aldrich, and H. S. White, *J.S.A.E.*, 1930, **27**, 93, 218; 1931, **28**, 315; 1931, **29**, 447.

matter, it having been found that when the concentration of gum exceeds a certain small value, trouble may be experienced from valve-sticking in certain engines. The concentration of gum in cracked gasolines is increased if the fuel is exposed to oxidation by blowing with oxygen or air. The additional product, or "potential" gum, in practice, is of less importance than the original, or "preformed" material. Gum concentrations are usually stated in milligrams of gum from 100 ml. of gasoline when evaporated to dryness. A motor spirit showing a preformed gum value of 30 mg./100 ml. gave rise to valve sticking. It appears, however, that such trouble has not occurred when the gum concentration has been below 20 mg./100 ml. The British Air Ministry requires a very high standard in freedom from gum, and a maximum residue of 0·01 per cent. or 8 mg./100 ml. only is allowed.

The presence of small proportions of sulphur is usually considered unimportant in automobile fuels, unless the quantity and nature of the compounds give rise to unpleasant smell. The British Air Ministry, in its specification for fuel, limits the total sulphur to 0·15 per cent.

Synthetic Hydrocarbons.

No attempt is made in these notes to discuss the problems relating to the production and use of fuels hydrogenated from coal. The technical and economic questions involved are most ably discussed in a treatise on the subject entitled "Coal," which was presented by Dr. W. R. Ormandy before the Institute of Fuel in October, 1931.

Co-operation in Development.

Engine development has, in a general way, proceeded in parallel with the evolution of engine fuel. It has been shown in these notes that the demand for greater power-output has led to the raising of anti-knock values, to enable the necessary higher compressions to be used.

More rapid advance could undoubtedly have been made had manufacturers of engines and producers of fuels established a closer co-operation, the necessity for which is only now being generally realised.

Gasoline Engine Design.

Although there are no revolutionary changes in engine design to report during the past two years, there is no doubt that considerable progress has been made.

In order to review these developments it will simplify matters if the various applications of the gasoline engines be considered separately.

(1) Motor Car Engines.

Considering first the number of cylinders, it is interesting to observe the tendency towards increasing the number of cylinders both on the Continent and in the United States, while in this country the 8-cylinder engine has practically disappeared and Daimlers are still the only producers of 12-cylinder models. The 4-cylinder engine has, however, now been passed in numbers by the 6-cylinder in the United Kingdom, the four being represented by only 30 per cent. of the total number of different models, compared with 60 per cent. by 6-cylinder models.

Crankcase and cylinders.—The increase in the number of small 6-cylinder engines has led to the integral construction of the crankcase and cylinders. This is a decided advantage both from the point of view of rigidity and the elimination of a stressed oil joint between the crankcase and cylinder block.

The accessibility of the valve tappets with this construction is improved, due to the fact that the size and position of the tappet chamber are not penalised by the horizontal joint. On the other hand the removal of pistons and connecting rods is rendered more difficult, with the integral construction, owing to the necessity of dismantling the big-end to allow the rod to be carried high enough up the cylinder bore to permit the withdrawal of the gudgeon-pin above the top face of the cylinder. The piston can then be removed from above, whilst the rod is taken out below. This difficulty does not exist if the big-end of the rod will pass up through the cylinder bore, but the tendency towards increased crankshaft scantlings generally makes this impossible, particularly in engines with more than 4 cylinders.

Cylinder wear has caused considerable attention to be given to the question of fitting removable cylinder liners, made in either centrifugally cast iron or Nitralloy steel.

Valves and Valve Gear.—The battle between poppet valves and sleeve valves is definitely going in favour of the poppet valves. The Knight double-sleeve valve engines are still produced by only some six manufacturers in all countries. The " Burt-McCollum " single-sleeve valve engine has made no headway so far as motor cars are concerned. This seems a pity, since there are great possibilities in this type, as is shown by its relatively greater use in other fields.

In poppet valve engines, whilst the trend in the United States is still in favour of the side valve or " L " head, in Europe the bias is in favour of the overhead valve type. This is mainly due to the small size of European engines, where the use of side valves would make the valve tappets very inaccessible. It is interesting to notice the tendency towards the adoption of the overhead inlet valve with the

side exhaust valve, the combustion chamber being concentrated over the exhaust valve, and the sparking plug centrally placed as shown in Fig. 5.

The steel manufacturers continue to improve the quality of valve materials, and silicon-chrome and nickel-chrome steels are generally used for exhaust valves. A valve cooled by means of a copper core, forged into the valve stem and head, and flowing well out towards the seat has recently been introduced in the United States. Valve guides fitted with graphite impregnated bushes are also being employed. Valve tappets are still represented by the flat, or "mushroom" type and by the round type. The latter shows a tendency to supersede the roller follower owing to its being lighter and having fewer wearing surfaces.

Camshaft and Auxiliaries Driving Gear.—The roller chain is returning to favour for camshaft and auxiliary drives, in both single and double roller form. The old trouble experienced with chains becoming slack is now overcome by improved lubrication and by the fitting of an automatic chain tensioner. There is a tendency to revert to the Vee belt for dynamo and fan drives, and the improved construction and simple application of these belts is no doubt responsible for their return.

Pistons.—Aluminium pistons are used almost exclusively, although a few manufacturers are fitting pistons with aluminium crowns and cast-iron or steel skirts. Improvements are noticed in oil-scraper rings which are now given more adequate passage ways for the return of the oil through the back of the ring grooves. The use of the fully-floating gudgeon pin is becoming more general, axial movement being limited by circlips or buttons.

Crankshafts and Main Bearings.—Increasing attention is being given to the necessity for adequate crankshaft scantlings and properly supported journal bearings. Crankshaft sizes are increasing accordingly to keep pace with the increase in engine speeds, and multiplicity of cylinders. Aircraft engine practice is reflected in recent automobile designs in the adoption of steel instead of gunmetal, as a backing for the white metalled main bearings.

Lubrication.—A pressure oil system is now used by most manufacturers, usually fed by a gear pump in the oil sump driven from the camshaft by means of helical gears. Increased pressures are being used in order to pass more oil through the bearings and so deal with the extra heat set up by the increased surface speeds in the bearings of the crankshafts and big-ends.

(2) Commercial Vehicle Engines.

In considering the modern omnibus engine, one is immediately struck by the great improvements made in recent years. The

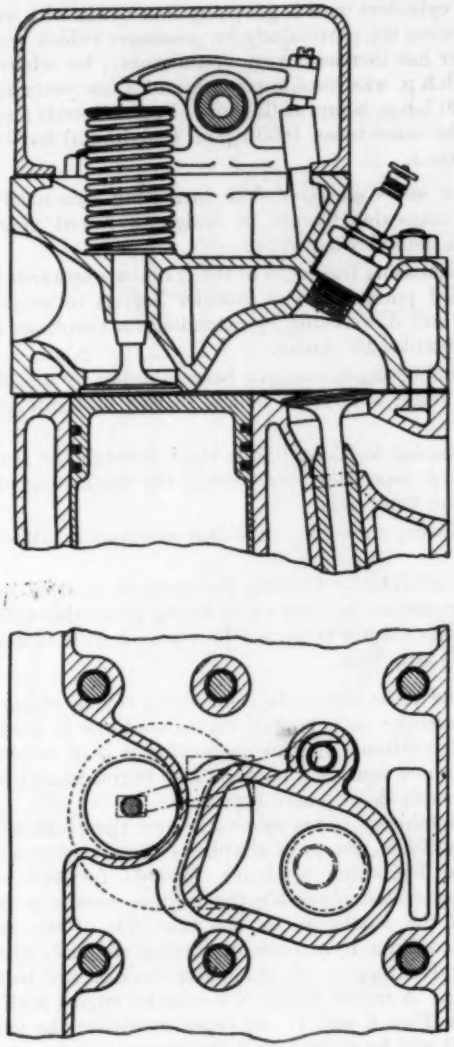

FIG. 5.

number of cylinders used is generally four or six with an increasing tendency to use six, particularly for passenger vehicle work. Engine horse-power has increased very considerably, for whereas between 50 and 70 b.h.p. was considered sufficient a few years ago, between 100 and 130 b.h.p. is now called for. Engine speeds also are higher in about the same ratio, 1800 r.p.m. (maximum) having increased to 3000 (max.).

Crankcase and Cylinders.—The increasing structural stiffness is the most noticeable feature of design in recent years. This is achieved in the following ways :—

(*a*) By increasing the depth of the crankcase upwards by allowing the uncooled portion of the cylinder barrels to project into the crankcase, and downwards by extending the crankcase casting well below the crankshaft centre.

(*b*) By connecting the engine bearers either by a stiff horizontal flange or, better still, by a hollow section cast integral with the crankcase.

(*c*) By passing horizontal bolts right through the crankcase and main bearing caps, thus overcoming the weakening effect of the arches in the bulkheads.

(*d*) By fitting monobloc cylinders adequately attached to the crankcase.

(*e*) Alternatively by forming the cylinder portion in one piece with the crankcase, in some cases fitting renewable cylinder liners, so that worn cylinder bores can be replaced without scrapping the main engine structure.

Valves and Valve Gear.—In commercial vehicle engines, as in the case of passenger cars, poppet valves continue to hold their well established position. In this connection it is of interest that the Daimler Co. now market a poppet valve engine in addition to their range of double-sleeve valve types.

The predominance of the side-valve over the overhead valve type is still in evidence, due to its simplicity of valve gear and camshaft drive. The increasing tendency towards forward control—the driver being seated alongside the engine—makes it necessary to arrange all the auxiliaries on the near side of the engine. The auxiliaries continue to increase in number and size, with the result that the valve tappets of side-valve engines are inclined to be inaccessible. A recent design of 6-cylinder engine with side valves is shown in Figs. 6 and 7. In order to render the valve tappets accessible it will be noticed that the magneto and water pump are mounted crosswise at the rear of the engine and driven by a helical gear from the camshaft wheel.

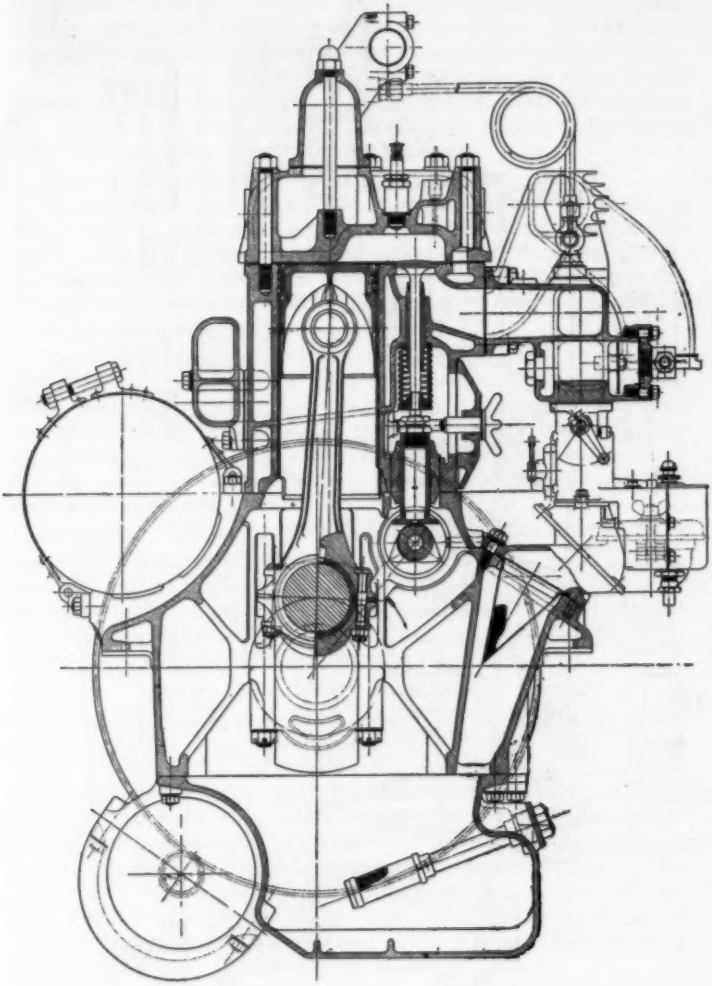

FIG. 6.

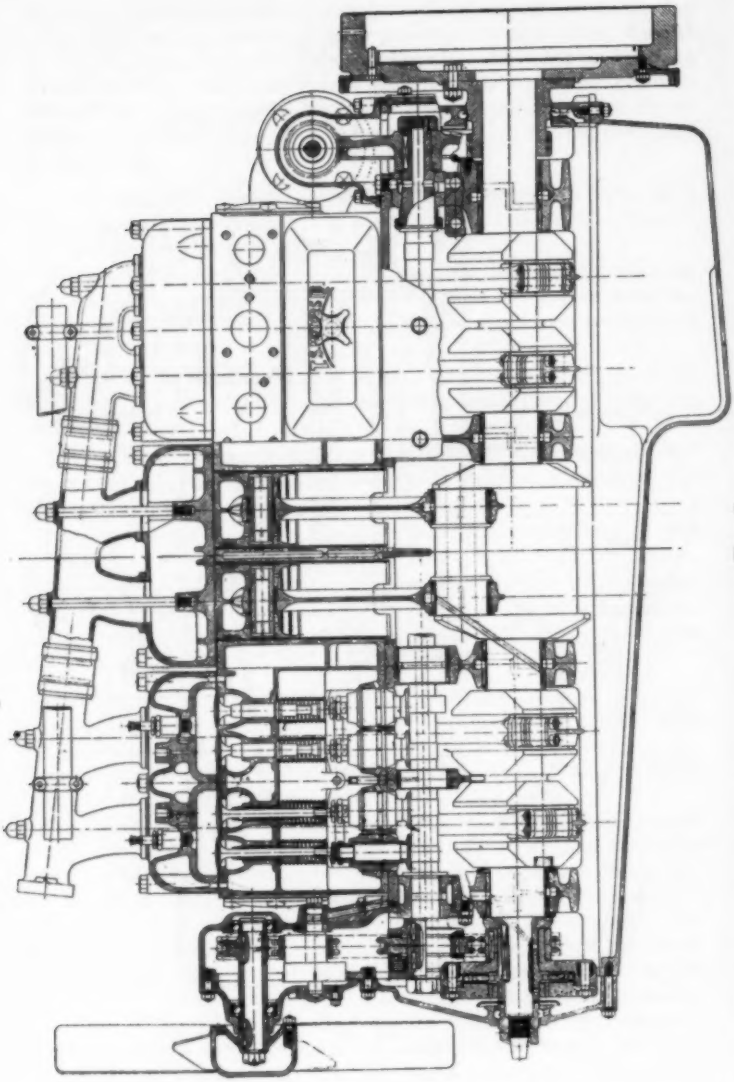

FIG. 7.

A very neat arrangement of overhead valve gear is that in which the camshaft is carried low down in the cylinder head with bell-crank levers operating the vertically mounted valves direct. This has been adopted by two of the largest and most successful manufacturers.

Renewable valve seatings are being embodied in some recent designs, and mention should be made of the use of special cast-iron flat tappets with the underside "chilled" in casting to provide a hard wearing surface in contact with the cam.

Camshaft and Auxiliaries Driving Gear.—Here also, as in the motor car engine, the roller chain is coming back into favour, in double or triple form, generally driven at the front end of the crankshaft. The new Daimler poppet valve engine is an exception, utilising as it does an inverted tooth or silent chain driven from the flywheel end of the crankshaft. The auxiliaries, however, are driven from the camshaft by triple roller chain.

Pistons and Crankshaft.—Pistons vary greatly both in material and design. The materials used are either cast-iron or special aluminium alloys. It is noticeable that many engine manufacturers are fitting pistons of proprietary makes. Progress in oil scraping and gudgeon pin design has followed lines similar to those described for the motor car engine. As in motor car engines, crankshaft sizes still tend to increase.

Lubrication.—Difficulty has been experienced in recent years due to the higher oil temperatures that naturally follow the increase in engine speeds. This problem has been dealt with by fitting an oil-cooling radiator under the water radiator, or in some instances by casting deep corrugations in the bottom of the engine sump, thereby providing additional surface for dissipating heat.

(3) Aircraft Engines.

Progress in aircraft engine design has been shown mainly in the improvement of details and by increasing power. There is still room both for the water-cooled "V" type engine, with its low head resistance, and for the air-cooled "radial" engine, with its simplicity of what the Americans so aptly term "plumbing." The outstanding event of last year is undoubtedly the development of Rolls-Royce "R" type engine used by Great Britain in the Schneider Trophy machine. The output of this engine for the race was increased to practically three times its previous power as rated for commercial purposes. Fig. 8 shows a photograph of the engine.

Considerable advance has been made by the extensive use of a new range of aluminium alloys containing small quantities of magnesium. In the forged condition one of these alloys is being used for pistons.

Crankcase and Cylinders.—The rigidity of structure has been improved for 12-cylinder "V" type engines by means of bolts passing right through the crankcase and main bearing caps, as is done in certain heavy vehicle engines. Through bolts, for attaching the cylinders and cylinder heads to the crankcase, are employed in order to remove longitudinal stress from the cylinders.

The general construction of the radial engine has not altered recently, but detail improvements in the finning of cylinder barrels and of heads are being introduced on the Bristol "Jupiter" engines in order to gain better cooling.

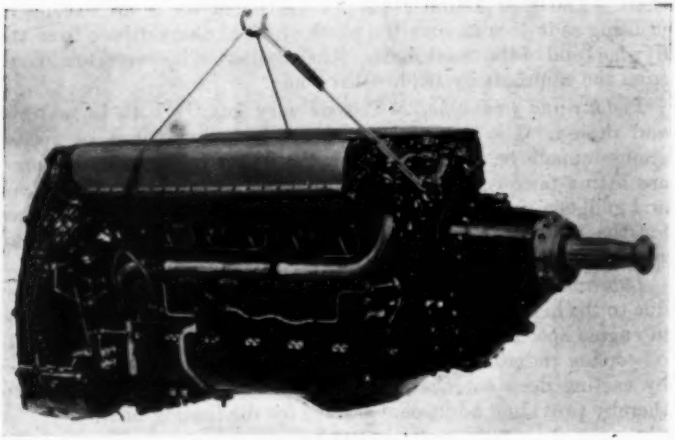

FIG. 8.

Valves and Valve Gear.—Sodium-cooled valves have been adopted by several manufacturers and these have completely overcome the previous difficulty due to preignition from hot exhaust valves. In this arrangement the valve is hollow and is partially, but not wholly filled with sodium. As it becomes molten at the temperatures attained while running, the sodium is thrown about inside the sealed space; heat is thereby transferred from the head to the valve-stem where the guide conducts it away. It is found that very ample lubrication of the valve guide is needed for these conditions.

A modification has recently been made to the valves of the Bristol "Jupiter" engines, the valve-stems being hardened on their working surfaces, thereby reducing the wear both on the stem and on the valve guides.

Camshaft and Auxiliaries Driving Gear.—A notable feature of the Rolls-Royce engines is the spring drive for the auxiliaries to prevent the torsional vibration at the rear end of the crankshaft from being transmitted to the supercharger and other auxiliary drives.

Supercharging is more extensively employed, being generally used to maintain power at altitude. The centrifugal type of blower is now almost universal and is driven through gearing from the engine crankshaft. Apart from increasing the power output of the engine, the supercharger usually assists carburation and equality in the distribution of fuel to the cylinders.

As the result of fuel improvements in anti-knock quality it has been possible to improve engine power-weight ratio either by increased supercharge or by raising compression ratio.

(4) Industrial Engines.

The main advance has been made by increasing engine speeds, and thereby increasing the power output for a given size and weight of engine. One reason for this increase in speed is due to the fact that the industrial engine market is being invaded by modified versions of production motor car engines.

(5) Motor Cycle Engines.

The most important development in the motor cycle industry is the 15s. tax concession for machines having engines not exceeding 150 c.c. capacity. This gives added stimulus to the " two-stroke " engine, as the simplicity and low cost of this type of engine makes it the most suitable power unit for such small cylinder capacity. Motor car practice is reflected in some of the new models which have four-cylinder engines ; a curious feature being that each of these engines has a different arrangement of cylinders. The Ariel " Square Four " has two crankshafts geared together, while the Matchless " Four " has two pairs of cylinders arranged in a narrow Vee on a two-throw crankshaft. The Brough " 4-in-line " has an Austin " 7 " car engine of increased capacity. Lubrication is now receiving more detailed attention in design. Dry-sump oiling arrangements are incorporated in recent models, and oil leads to valve guides are more common.

In conclusion, the authors desire to express their thanks to the Asiatic Petroleum Co., Ltd., the Anglo-Persian Oil Co., Ltd., Mr. J. Kewley, Mr. C. H. Barton and Mr. R. A. Eldridge for their valuable assistance in preparing the section which deals with gasoline, and particularly to Mr. R. Stansfield and Dr. S. F. Birch for the assistance given in collecting data and for permission to publish their results of tests on pure hydrocarbons. Acknowledgment is also made of the courtesy of Messrs. Rolls-Royce and Messrs. T.S. Motors for permission to include photographs and drawings of their engines.

Gum Formation and Its Inhibition in Motor Spirits.

By W. H. Thomas, A.R.S.M. (Member).

INTRODUCTION.

The subject of gum inhibitors for use in motor spirit has not hitherto been dealt with specifically in previous Reports on the Progress of Naphthology. The following remarks, therefore, cover a somewhat wider period than the years 1930 and 1931, in order to present as complete a picture of the subject as possible. The increase in the use of vapour-phase cracking processes for the conversion of heavy oils into anti-knock motor spirit[1], with the consequent importance of producing a gum-stable product, has resulted in considerable interest being taken in the action and use of inhibitors of gum formation. Although the latter had been studied to some extent prior to 1928, the work of the Benzol Research Committee[2], published in that year, focussed the attention of petroleum technologists on a means whereby the losses of volume and engine test occasioned by the refining and stabilisation of cracked spirits might be substantially reduced.

Apart from their use for reducing the gumming tendencies, colour increase and engine test decrease of motor spirit, inhibitors have been used or suggested for preventing (*a*) the deterioration of rubber, soap, etc.[3, 4, 5, 6]; (*b*) the oxidation of mineral wax[17, 18], greases[19], and lubricating (transformer) oil[7, 8, 9, 10, 11, 12]; (*c*) the oxidation and development of acidity in insecticides[15]; and (*d*) gum formation in gas distributing systems[16], and Backstrom[20] has discussed the inhibiting effect of alcohols on the oxidation of sodium sulphite.

The study of the practical application of inhibitors to the stabilising of cracked spirits necessitates the development and standardization of a stability or oxidation test for the evaluation of the efficacy of these materials. A number of such tests have already been evolved[2, 21, 22, 23, 24, 25, 26, 27, 28], but up to the present no universally applicable method has yet been agreed upon.

Theories of Gum Formation.

As long ago as 1922, Smith & Cooke[29], in a study of various methods of evaporation and oxidation of cracked gasolines, came to the conclusions, firstly, that gummy and resinous deposits are caused by oxidation and have no direct relation to unsaturation as determined by solubility in sulphuric acid, and, secondly, that gums are polymerised aldehydes which are probably formed by oxidation of olefines.

It is now generally accepted that gum formation in cracked spirits is due to some type of oxidation involving the development of peroxides as an intermediate stage. Callendar[30] has shown that these peroxides induce knocking, while Mardles and Moss[32] have discussed the acceleration of gum formation by aeration, increase in temperature and the action of actinic light. They have explained the reasons for the deterioration in anti-knock value of a spirit during gum formation.

In a paper by Dumanois, Mondain-Monval and Quanquin[31], it is shown that by air oxidation at 300° C. of pentane, hexane, or gasoline vapour, an oily substance is formed which contains peroxides and yields aldehydes on heating. It is considered that the peroxides belong to the series R.O.O.H., the mono-methyl and ethyl members at least being present.

Brooks[32] regards the aldehydes, organic acids, ketones, water, etc., which accumulate in cracked spirit on exposure to air and sunlight, as the decomposition and reaction products of organic peroxides, the decomposition occurring according to the equation

$$\rangle C{=}CH_2 + O_2 \rightarrow C(-O-O)-CH_2 \rightarrow \rangle C{=}O + HCHO.$$

He considers that, although condensation products of aldehydes might be a contributory cause of gumming, the main cause appears to be by the action of organic peroxides through polymerisation.

Kogerman[33], attacking the problem from a somewhat different angle, studied the behaviour of four diolefins, and concluded that the main reaction proceeding during auto-oxidation is really an addition of oxygen and that only in special cases does polymerisation play an important part. A study of suitable anti-catalysers, he said, would lead to the discovery of compounds which stabilise cracked gasoline.

The gumming tendencies of pure olefines in gasoline has been studied by Cassar[34] together with their reactions with certain reagents, while Flood, Hladky and Edgar[35] have investigated the chemical nature of gum-forming constituents in gasoline.

The term " pseudo-gum " has been applied to the gum-forming constituents in gasoline by Wagner and Hyman[36], who show that pseudo-gum consists largely of peroxides, peracids, aldehydes and ketones.

Further work on the chemistry of gum formation is that of Story, Provine and Bennet[37], who consider that peroxides are first formed as intermediate compounds, the end products being acids in the form of anhydrides, lactones, etc., water and carbon dioxide.

In a very informative paper on peroxides and gum in gasoline, Yale and Wilson[38] have given details of a method of determining the peroxide content of cracked gasolines, and investigation of the properties of peroxides leads them to conclude that gum is usually present as peroxides, which decompose and polymerise to true gum on evaporation.

The Action of Inhibitors of Gum Formation.

From the above it will readily be appreciated that in order to avoid gum formation in gasolines, it is necessary to prevent the condensation, polymerisation or oxidation of the unsaturated bodies, brought about by the presence or formation of peroxides.

A stable product may be obtained by suitable chemical or polymerising treatment with reagents such as sulphuric acid, fuller's earth, zinc chloride, etc., but, as has already been pointed out, the relatively heavy treatments required result in a loss of volume and engine test. It is possible, however, by the addition of small amounts of certain "inhibitors" to delay very greatly the formation of these gums, and if this can be accomplished for a sufficiently long period, the necessity for removal of the gum-forming substances with the attendant losses is obviated. It is to be noted that gum-inhibitors do not prevent gum formation but only create a delay period before gum formation commences.

Although the chemistry of gum formation has been studied to a considerable extent, there appears to be little published work dealing with the mechanism of the action of gum inhibitors. The work of Moureu and Defraisse[39] on the inhibiting action of various substances on the oxidation of organic substances has a direct bearing on the use of inhibitors, for they examined the effect of added substances on the rate of oxygen absorption by single oxidisable substances.

Smith and Wilson[40] investigated the action of inhibitors on the rate of oxygen absorption by unsaturated organic compounds; while Backstrom[20], Alyea[41], and Christiansen[42] have all suggested a chain reaction to account for the anti-oxidation effects of inhibitors. In discussing the inhibiting effect of alcohols on the oxidation of sodium sulphite, Backstrom shows that the alcohol itself is oxidised, and that there is a marked similarity between thermal reactions and light reactions. The latter are shown to be chain reactions, and hence inhibition of a thermal reaction probably also acts by the breaking of chains. A high concentration of inhibitor merely shortens the chains, but does not affect the amount of inhibitor used up, while in both light and dark, the chain lengths are the same.

Inhibitors of Gum Formation.

Many compounds have been suggested for use as inhibitors not only of gum formation but also of colour increase and engine test (anti-knock) decrease.

In the investigations concerning the use of inhibitors for the stabilisation of benzoles, the Benzole Research Committee[2], [26] has worked mainly on tri-cresol (a freshly distilled phenolic fraction boiling over a range of 195°–203° C., and having a low sulphur content), although other materials—*e.g.*, aniline, phenol, etc., have received a certain degree of attention. Only minute amounts (0·03 per cent. by wt.) of tri-cresol have been found to be necessary for the stabilisation of benzoles. It is shown that benzoles stabilised by an inhibitor are little inferior to those purified by acid, and that dilution of unstabilised benzole with petrol retards resinification to a greater extent than would be accounted for by the concentration of unsaturated compounds.

On the other hand, Mardles and Moss[22] state that the effect of blending cracked spirit with straight run spirit does not always result in a decrease of gumming rate in proportion to the dilution.

Egloff, Faragher and Morell[43] found that the addition of 0·1 per cent by weight of aniline, hydroquinone, naphthaline or anthracene to a cracked gasoline will inhibit decrease of anti-knock value, and that the efficacy of each of these four inhibitors varies somewhat with different gasolines. Naphthalene, urea, pyrene, phthalic anhydride and carbazole (0·1 gm. per 100 ml.) were found to inhibit the formation of gum on exposure to sunlight for 24 hours, but in one instance urea acted as an accelerator of gum formation. With regard to colour stabilisers, it was found that the action of any particular inhibitor varied considerably with different gasolines, among the most effective being gum camphor, urea, phenanthrene, pseudo-cumene, acenaphthene, α and β methyl-naphthalene, anthracene, naphthalene, fluorene, tetralin, phthalimide and phthalic anhydride.

The action of inhibitors on gasolines prepared from a Dubbs pressure distillate has been examined by Sullivan[44]. Anthracene, gum camphor, an inhibitor known as Du Pont No. 2, and aniline were added to separate portions of these gasolines in the proportion of 1 lb. to 8000 gallons, and deterioration of colour on standing in sunlight, dissolved gum by dish method and accelerated ageing tests determined on the whole series. The effect on colour stability was found to vary according to the gasoline, but anthracene and Du Pont No. 2 generally caused an improvement. Aniline accelerates colour formation, but all the other inhibitors decrease the gum content of the untreated sample. Whereas with the treated samples, anthracene and Du Pont No. 2 generally give improvement, gum camphor accelerates gum formation.

The work of Egloff, Morell, Lowry and Dryer[45] was undertaken for the purpose of finding inhibitors which would stabilise colour, gum and knock rating in certain gasolines and of correlating the inhibiting action of chemical substances with their structure. The work is also a combination of studies on gasoline in storage and gasoline exposed to an accelerated ageing test. The first section deals with the results on inhibitors in the oxygen bomb and in storage over a period of three months, the inhibitors being tricresol, hydroquinone, Du Pont No. 8 and α naphthol. It would appear that there is a definite correlation between the increase in induction period in the bomb produced by an inhibitor and its value in protecting stored gasoline against increase in gum and depreciation in knock rating.

In the next section of the work, approximately 150 substances of varied chemical constitution were studied by means of the bomb to determine their inhibiting qualities, a uniform concentration of 0·05 per cent. of inhibitor being used in practically all cases.

The results of the tests on a large number of phenolic compounds show that the weak inhibiting action of phenol itself is intensified by the introduction of certain specific groups into the ortho or para position. Thus *o* or *p* cresol has considerably more inhibiting action than phenol, while ortho and para amino phenols rank with the best inhibitors known. The meta derivatives of phenol are not very effective, and this is also seen on comparing the long induction period of pyrogallol with the shorter time of phloroglucinol. α naphthol is superior to the β compound, but the hydroxy-diphenyls tried had weak inhibiting action.

It was found that while the amino group in the amino phenols intensified the inhibiting action of phenol, the amines as a group were relatively poor inhibitors. The aromatic halogen compounds showed no stabilising influence unless some known inhibiting group was also present, and of the hydrocarbons investigated only fluorene and tetralin increased the induction period.

The aromatic ethers studied did not increase the induction period except when there was an amine group present, while the ketones, amides and nitro compounds used had little effect. Little or no effect was obtained by the use of amides and nitro compounds, acids, nitrogen and sulphur compounds, alcohols or terpenes.

British Patent Literature Dealing with Inhibitors of Colour and Gum Formation.

Reference has already been made in the introduction to patent literature dealing with the inhibition of deterioration (*e.g.*, oxidation) of rubber, insulating and lubricating oils, soaps, greases, wax, insecticides, etc., by the addition of small amounts of suitable anti-oxidation agents.

Many of the patents quoted appear to be equally applicable to cracked gasolines, but those dealt with in the following remarks are designed essentially for the stabilisation of cracked gasolines.

For the sake of brevity it is proposed to give only short abstracts of these patents as follows :—

SOMERVILLE, E.P. 289,347, 26.10.26.—Gum stability in motor fuels containing unsaturated hydrocarbons is effected by means of the addition of a suitable quantity of an aromatic amine, or phenol, or nitro compound. Before the addition of the stabiliser, gumming accelerators, unsuitable concentrations of inhibitors and resin are removed.

JOHNSON, E.P. 312,774, 30.4.28.—This patent deals with a process of inhibiting colour formation in kerosine or gasoline due to auto-oxidation, by the addition of an aromatic or aliphatic dihydroxy compound, an aromatic amine or polyphenol, urea or urea derivative or an alkaloid. The addition is insufficeint in amount (1 part in 10,000) to colour the distillate.

STANDARD OIL DEVELOPMENT CO., E.P. 318,521, 3.9.29.—Formation of gum in motor spirit is inhibited by the addition of less than 5 gms. per gallon of pyrogallol.

STANDARD OIL DEVELOPMENT CO., E.P. 319,362, 19.9.29.—Gum formation in cracked gasolines is reduced by the addition (less than 1 gm. per litre) of an aromatic compound with condensed nuclei (alpha naphthol) having an alpha substituted group which is able to combine with acids. The hydrocarbon may also contain a small quantity of a metal carbonyl or organometallic compound in addition to the aromatic compound.

STANDARD OIL DEVELOPMENT CO., E.P. 319,363, 19.9.29.—Gum stability in cracked spirit is effected by the addition (less than 1 gm. per litre) of a small quantity of an aromatic hydrocarbon with condensed nuclei (anthracene) and an aromatic compound with condensed nuclei having an alpha substituted group (alpha naphthol) which is able to combine with acids.

HOWES, SCOTT AND IMPERIAL CHEMICAL INDUSTRIES, E.P. 336,515, 22.7.29.—Light hydrocarbons are distilled in the presence of ammonia. This treatment is claimed to stabilise the distillate as regards colour and gum. It is preferable not to remove the ammonia immediately after distillation since its presence tends to inhibit colour and gum formation.

STANDARD OIL CO., E.P. 348,011, 29.10.29.—This patent refers particularly to discoloration and colour stabilisation of gasoline and kerosine. An organic reducing agent is added (less than 0·25% by wt.) in a proportion insufficient to impart colour, but sufficient to decolorise the oils and prevent rediscoloration and formation of odour. The reducing agent may be an organic hydroxy, dihydroxy or trihydroxy compound of the benzene or naphthaline series (*e.g.*, hydroquinone, orcinol, pyrogallol, α or β naphthol, etc.). The following materials may also be used :—Thiourea, thiocarbanilide, aromatic amines, phenyl diamine, phenyl hydrazine, oxalic acid, stannous oleate, sodium methylate, stannous chloride, etc., the solid reducing agents being dissolved in aliphatic alcohol.

STANDARD OIL CO., E.P. 349,427, 21.11.29.—A method is described for imparting colour, gum and odour stability to motor fuels and for removing any objectionable colour developed during storage. An addition is made to the gasoline of less than 0·1 per cent. of a 10 per cent. solution of a poly hydroxy benzene (pyrogallol) in an aliphatic alcohol.

STANDARD OIL CO., E.P. 350,438, 5.3.30.—Gum stability in cracked (vapour phase) spirits is effected by the addition of a substituted aminophenol (less than 0·05 per cent. by wt.), *e.g.*, methylaminophenol or benzylamino phenol.

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Kerosine and White Spirit.

By Walter A. Woodrow, A.I.C., F.C.S. (Member).

A study of the period under review shows that while important developments have occurred in methods of refining, relatively little work has been published in other respects as regards kerosine.

With regard to burning tests for kerosine, the Standardisation Committee of the Institution of Petroleum Technologists has formed a Sub-Committee to deal with the "Tendency to Smoke" test, and consideration has been given to the design of a suitable lamp for this purpose. It is, therefore, hoped that in the near future a suitable test for the determination of this characteristic property will be available.

Refining.

An interesting study of the behaviour of the various types of hydrocarbons, more especially aromatic hydrocarbons on the illuminating properties of burning oils, has been made by Danaila, Stoenescu and Dinescu[1]. The effect of illuminating power was studied using a small Louchaire type of lamp, and it was shown that the illuminating power of kerosine containing only saturated hydrocarbons was lower than that of synthetic mixtures containing aromatic hydrocarbons. It is further stated that the presence of aromatic hydrocarbons increases the intensity of the flame, and it is only when the aromatic hydrocarbon-content exceeds a certain limit that a decrease in the illuminating power occurs. The proportions of aromatic hydrocarbons necessary to give the best results vary from oil to oil, although it is also stated that a correct type of lamp is essential in each individual case, which would appear to limit the applicability of their results.

They conclude that the deficiencies in the illuminating powers of Rumanian burning oils are to be attributed to the type of lamp used rather than the high aromatic hydrocarbon-content. These authors also investigated the effect of refining agents, including bleaching earth, sulphuric acid and liquid sulphur dioxide, reaching a conclusion contrary to that normally accepted, that it is preferable in the refining of kerosine not to reduce the aromatic hydrocarbon-content. Further comparison was made between kerosine and the same kerosine to which varying quantities of cetene (Hexadecylene) had been added, and they conclude that even a very small percentage of olefine hydrocarbons can decrease the illuminating power of a burning oil.

[1] Danaila, Stoenescu and Dinescu, *Petr. Z.*, 1930, **26**, 47.

Brandt[2] and Cattaneo[3] have made a study of the Edeleanu process, the latter author emphasising the great advantage obtained from the use of sulphur dioxide, whereby aromatic and unsaturated hydrocarbons, which are undesirable in kerosine fractions, can be easily removed and subsequently recovered for other useful purposes, whereas acid treatment removes these constituents giving acid tar and a definite "refining loss." Again, the refining agent, *i.e.*, sulphur dioxide is easily and completely removed from the finished kerosine. A very complete description of the process and plant is given, showing how thoroughly this process has been perfected.

The single plant Edeleanu unit operated at the Los Angeles refinery of the Union Oil Company is believed to be the largest in the U.S.A. (Willson[4]). This plant is a 900-ton unit, capable of treating 7000 barrels of kerosine distillate per day. Apparently the refining of Californian kerosine distillate by this process is much more economical than acid refining.

The results of hydrogenation of suitable petroleum products for the formation of kerosines of excellent burning quality is described in an article by Haslam and Russell[5]. Water white kerosines can be produced from inferior kerosine distillates and poor quality light gas oils. Experiments have shown that best yields are obtained from stocks having slightly more viscosity than that required for the finished kerosine, yields of from 65 to 85 per cent. being obtained. Hydrogenation reduces the sulphur-content, lowers the specific gravity and, although the chemical composition of various charging stocks may differ widely, analyses of finished kerosines indicate olefines to be almost absent, and the major portion of aromatic hydrocarbons to have been converted into naphthenes and paraffins, and that there is no apparent effect on the naphthenes.

Rather and Beard[6] have described a method for preventing discoloration and the formation of bad odour on storage of kerosine by forcing an inert gas through a finely divided stream of the kerosine, thereby removing the air present. It is claimed that undesirable sulphur compounds can be removed from kerosine fractions by spraying with an ammoniacal solution of copper hydroxide under atmospheric conditions, the odour and colour being improved by this treatment (Muhlenberg[7]).

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[2] Brandt, *Ind. Eng. Chem.*, 1930, **22**, 218.
[3] Cattaneo, *J.I.P.T.*, 1930, **16**, 581.
[4] Willson, *Oil and Gas J.*, 25.12.30, **29** (32), 38, 131.
[5] Haslam and Russell, *Ind. Eng. Chem.*, 1930, **22**, 1030.
[6] Rather and Beard, U.S.P. 1,776,598.
[7] Muhlenberg, U.S.P. 1,750,420.

Good yields of kerosine can be obtained from Grozny Mazout, Orlov[8], by heat treatment in chromium-nickel-steel retorts at temperatures of 440–460° C. with hydrogen under a pressure of 70–265 atmospheres for 1–1½ hours.

In a patent by Robinson[9] a superior kerosine (50–54° Bé) is said to be produced by cracking or pyrolytic decomposition of paraffin from petroleum, shale-oils or low-temperature carbonisation plants. The kerosine produced is recommended as specially applicable for use in signal lamps.

The removal of colour from kerosines which have become discoloured during storage is claimed to be achieved by treatment with various organic and inorganic reducing agents, such as pyrogallol, α or β naphthol, oxalic acid, stannous oleate, etc.[10].

Catlin[11] suggests different treatments for various forms of sulphur impurities in petroleum distillates.

Properties.

An important article, following on the work described in a paper by Jackson and Kewley[12] has been presented to this Institution by Minchin.[13] It deals with the important question of "Tendency to Smoke" of kerosine, with special reference to the connection between this characteristic and chemical composition. Minchin found that a definite relationship existed between "tendency to smoke" with aromatic hydrocarbons and naphthene contents, and also with aniline solution point. One interesting indication was that curves obtained for "tendency to smoke" of pure aromatic hydrocarbons and naphthenes crossed the ordinates at exactly the same place.

A study of homologous series showed that except for the paraffin hydrocarbons, "tendency to smoke" decreases with the increase in the number of carbon atoms, in other words with increase of boiling point.

Downer[14] has devised an ingenious type of constant level consumption meter which should prove to be very useful in kerosine research.

The mean Molecular weights, Specific Heats and Total Heats of various kerosine fractions are included in the papers by Lang, Jessel and Steed[15], also Lang and Jessel.[16]

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[8] Orlov, Ipatev and Bielopolski, *Brenn.-Chem.*, 1929, **10**, 346.
[9] Robinson, U.S.P. 1,809,183.
[10] Standard Oil Co., E.P. 348,011.
[11] Catlin, *Refiner*, 1930, **9**, 95.
[12] Jackson and Kewley, *J.I.P.T.*, 1927, **13**, 372.
[13] Minchin, *ibid.*, 1931, **17**, 102.
[14] Downer, *ibid.*, 1931, **17**, 242.
[15] Land and Jessel and Steed, *ibid.*, 1930, **16**, 783.
[16] Lang and Jessel, *ibid.*, 1931 **17**, 572.

Duff[17] discusses the connection between I.P.T. gravity temperature correction constants and the coefficients of expansion of petroleum oils.

Investigations have been made by Kanning and Brown[18] into the question of the most suitable decomposition temperature for a light kerosine fraction (200–230°C.) when passed over such catalysts as cobalt, iron, nickel or manganese.

It was found that the ability of the catalysts to decompose the kerosine can be accepted in the order as given here, and also that the most favourable temperatures varied with the catalyst, this also applying to the types and amounts of hydrocarbons in the gaseous products.

Chemical Composition.

It has recently been stated, Poth, Schulze, King and others,[19] that Californian crude kerosine distillate is an excellent source of material for nitrogen compounds. The authors showed that 50 litres of organic bases could be obtained from 150 barrels of this crude kerosine. The structure of one base was established as 2, 3, 8 trimethyl quinoline and the synthesis of this compound was effected.

In a description of a method for evaluating crude oils, Beiswenger and Child[20] give some details of an interesting and useful method for the estimation of kerosine. The method briefly consists of the production, in a specially devised still and fractionating column, of kerosine with a viscosity of 400 seconds (Saybolt Thermo-viscosimeter), the actual yield of kerosine being obtained by calculation.

By this method, the experimental work necessary for the estimation of quality and grade of kerosine in a crude oil is very much simplified. The yields obtained may be correlated with refining equipment, and thus a very reasonable prediction can be made from a work-up of a new sample of new crude oil.

White Spirit.

In France efforts have been made to compel exclusive use of turpentine in place of white spirit which is steadily increasing in demand. This policy is more in the interests of the turpentine industry than due to any shortcomings of white spirit.[21]

A controversial piece of work has been carried out by Masseille[22] who made comparative tests between turpentine and white spirit

[17] Duff, *ibid.*, 1930, **16**, 501.
[18] Kanning and Brown, *J. Phys. Chem.*, 1931, **35**, 2689.
[19] Poth, Schulze, King, Thompson, Slagle, Floyd and Bailey, *J.A.C.S.*, 1930, **52**, 1239.
[20] Beiswenger and Child, *Ind. Eng. Chem., Anal. Ed.*, 1930, **2**, 284.
[21] *Oil and Colour Trades J.*, 1930, **78**, 359, 1353.
[22] Masseille, *Peintures, Pigments, Vernis*, 1930, **7**, 1193, 1219, 1244; *Oil and Colour Trades J.*, 1930, **78**, 512.

by preparing white paints of various consistencies using each product, and applying these paints to different types of surfaces. No difference was observed regarding ease of application or covering power between the paints, but it is alleged that after a few months the white spirit paints became slightly yellow. Another objection to white spirit was that after six months storage thickening and change of colour of the paints had occurred. However, on account of its cheapness and in some cases superiority, white spirit has been preferred to turpentine by some French Government departments.

Jordan[23] in reply to the previous reference, states that the white spirit as used by Masseille was a low-flash, low-boiling paraffinoid mixture which did not conform to the English paint manufacturers' conception of white spirit (B.E.S.A. Spec. Type 1—White Spirit), hence giving a false impression of the behaviour of white spirit as compared with turpentine.

It is pointed out that whilst there is no doubt that turpentine is an excellent varnish-making material, on the other hand white spirit has in certain circumstances, definite and positive advantages, not the least of which is consistency in composition and quality.

[23] Jordan, *Oil and Colour Trades J.*, 1930, **78**, 1848.

Lubricants.

By E. A. Evans, F.C.S. (Member).

The advent of 1930-31 heralds a marked determination by several enthusiastic workers to synthesize lubricants both on a laboratory scale and on a production scale. Whatever results may have been obtained or whatever overlapping there may have been, sympathy and encouragement should be meted out to the investigators in this field for their boldness in undertaking a research which has claimed the attention of many speakers, but, alas! too few workers.

Abel in 1877 was granted British Patent 4769 for the production of oily products by the condensation of unsaturated hydrocarbons with aromatics in the presence of aluminium chloride. Lately Nash, Stanley and Bowen[1], and Stanley[2], have published the results of their work on the production of synthetic lubricating oils by catalytic polymerization of ethylene, preferably with aluminium chloride. In 1928, Dunstan investigated the use of other metal halides, and in 1930 Leamon was granted several patents in the U.S.A.[3] Morgan, Ingleson, and Taylor[4] used zinc chromite as the polymerizing catalyst. Stanley[5] has studied the use of sulphuric acid as a polymerizer. Elkington has been granted a British patent[6] to effect polymerization by the action of heat and pressure.

Sullivan, Voorhees, Neeley and Shankland[7] have prepared a comprehensive paper on their chemical and physical properties.

Synthetic lubricating oils have also been prepared by hydrogenation. Owing to the flexibility of hydrogenation of petroleum no sectional report can be considered complete without reference to it. Haslam and Russell[8] review the recent developments using pressures at about 3000 lbs. per sq. in. The oil and previously compressed hydrogen are mixed together, and delivered through heat exchanges to a coil furnace, thence to a catalyst-containing vessel. The degree of hydrogenation is controlled depending upon the results desired. Much of the sulphur in the

[1] *J.I.P.T.*, 1930, **16**, 830.
[2] *J.S.C.I.*, 1930, **49**, 349 T.
[3] U.S.P. 1,769,791-1,769,795.
[4] *Petr. Times*, 1930, **24**, 1024.
[5] *J.S.C.I.*, 1930, **49**, 349 T.
[6] E.P. 331,186, 1930.
[7] *Ind. Eng. Chem.*, 1931, **23**, 604.
[8] *Ind. Eng. Chem.*, 1930, **22**, 1030-1037.

oil is converted into hydrogen sulphide. By hydrogenation it is possible to make marked improvement in a number of inferior lubricating distillates.

Oils produced by hydrogenation are called hydrolubes.

White oils[9] are prepared by treating suitable petroleum products at 675°–850° F. with hydrogen at 50–200 atm. The reaction may be assisted by a catalyst comprising 90 per cent. chromium oxide and 10 per cent. molybdenum oxide.

Of the artificial lubricants may be mentioned "Oil-film."[10] Unfortunately its composition is not disclosed. Auer[11] claims to modify the physical properties of mineral oils by interaction of fatty oils with aromatic amines, and dispersing or dissolving the product in mineral oil. The I.G. Farbenind A.-G.[12] enhance the viscosity by addition of cellulose naphthenate.

Fluorescence in mineral lubricating oils can be removed by small amounts of gaseous sulphur dioxide.[13] The conclusion is that the action is chemical. Trautzl[14] disputes the conclusion and maintains that the phenomenon is optical. Tausz and Rabl[15] confirm their opinion.

Most investigators agree that the empirical formula for lubricating oils may be represented by the series C_nH_{2n-2} to C_nH_{2n-20}, Penna oils being in the neighbourhood of C_nH_{2n-8}. Davis and McAllister[16] state that Penna oils are mainly free from unsaturated hydrocarbons, but consist chiefly of groupings of paraffin chains with naphthene rings. Bestushev[17] fractionated some Russian oils and tabulated their characteristics.

Contrary to indications from Hildebrand's work on solubility, Ferris, Birkhimer and Henderson[18] found that no obvious relationship existed between internal pressure and dielectric constant and suitability of solvent when investigating solvent extraction of lubricating oils. Poole[19] has continued his work on the solubilities of oils and waxes in organic solvents with the object of supplying information for the separation of paraffin wax from liquid hydrocarbons.

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[9] Standard Oil Development Co. and F. A. Howard, E.P. 308,297, 10.6.30; *J.I.P.T.*, 1930, **16**, 348 A.
[10] *Petr. Z.*, 1930, **26**, 50; *J.I.P.T.*, 1931, **17**, 25 A.
[11] E.P. 337,751, 1929.
[12] E.P. 337,639, 1929.
[13] Tausz and Rabl, *Erdöl u. Teer*, 1931, **7**, 106.
[14] *Erdöl u. Teer*, 1931, **7**, 193.
[15] *Erdöl u. Teer*, 1931, **7**, 384.
[16] *Ind. Eng. Chem.*, 1930, **22**, 1326.
[17] *Erdöl u. Teer*, 1931, **7**, 159, 191, 205.
[18] *Ind. Eng. Chem.*, 1931, **23**, 753.
[19] *Ind. Eng. Chem.*, 1931, **23**, 170.

A useful catalogue of the metallic constituents of crude oil is compiled by Shivey.[20]

Barr's masterly treatise on Viscometry is a welcome addition to the subject. Winning[21] has designed a metal adaptor to slide into the Saybolt Universal viscometer so as to reduce the volume from 80 ml. to 15 ml. The operating conditions are standard. The time for 8 ml. of oil to flow into a graduated flask is measured. The conversion factor varies from 6·84 to 7·57 according to the viscosity of the sample. When using the standard apparatus the time can be reduced by measuring the efflux time of 28·6 ml. and multiplying the result by 3. Genereaux[22] gives the viscosity of a number of gases and fluids over a wide range of temperatures, and explains how to extend its use to other liquids. A modified equation for the viscosity-temperature relationship of lubricating oils has been suggested by Sloane and Winning[23] :—

$$\log \eta k = \frac{C}{t+135} + A$$

Houghton and Robb[24] have produced an alignment chart for estimating viscosity-gravity constant of petroleum lubricating oils. Extensive conversion tables for kinematic viscosity and the results obtained by the use of the various commercial viscometers is given by Woog.[25] The complete behaviour of an oil with changing temperature is defined by Walther[26] if a constant "m" and the viscosity at, say, 50° C. be stated. Further tables of approximate relationships between the various units have appeared.[27] Baillie[28] deals very fully with viscosity temperature relations and gives conversion tables for conversion of Redwood time into kinematic viscosity. A table is given by Freund[29] by which the viscosity in centipoises can be calculated from the viscosity in degrees Engler for oils having a higher viscosity than 8° E. The formula is $\eta = 7{\cdot}6$ Ed where η = viscosity in centipoises, E = degrees Engler and d = density. Efforts to utilise the falling ball viscometer for opaque fluids has claimed the attention of Moore and Cuthbertson.[30] The accurate timing of the fall of a steel or aluminium ball between two coils is made by the use

[20] *Ind. Eng. Chem.*, 1931, **23**, 1151.
[21] *Ind. Eng. Chem. Anal.*, 1930, **2**, 417.
[22] *Ind. Eng. Chem.*, 1930, **22**, 1382.
[23] *Ind. Eng. Chem.*, 1931, **23**, 673.
[24] *Ind. Eng. Chem., Anal.*, 1931, **3**, 114.
[25] *Ann. des Comb. Liq.*, 1930, **5**, 805 ; *J.I.P.T.*, 1931, **17**, 291 A.
[26] *Erdöl u. Teer*, 1931, **7**, 382 ; *J.I.P.T.*, 1931, **17**, 465 A.
[27] *Rev. Petr.*, 1930 (365), 435.
[28] *J.I.P.T.*, 1930, **16**, 643.
[29] *Petr. Z.*, 1930, **26**, *Motorenbetreib*, **10**, 3.
[30] *Ind. Eng. Chem. Anal.*, 1930, **2**, 419.

of an oscillator. It is suitable over a relative viscosity range between 2 and 200 poises.

Tausz and Rabl[31] state that the value of x in the expression ηx undiluted$=\eta$ diluted, is a measure of the viscosity dilution where η is expressed in centipoises and the oil is diluted by means of a solvent. Results are given of the viscosity dilution measurements of mineral oils, etc. Viscosity determinations at low temperatures have been made by Schlenker[32] using Vogel's U-tube apparatus.

Ordelt[33] states that the lubricating qualities of oils can be improved from the point of view of flattening the viscosity-temperature curve by the addition of paraffin up to a max. of 1–2 per cent. This change is confirmed by the rise in value of the Tausz exponent x (η dil. oil$=\eta$x undil. oil). Temperature-viscosity data are given for commercial paraffins and ceresins of different melting points. Viscosity is dependent upon melting point and not upon closeness of fractionation or manner of refining.

The fifth report of the A.S.M.E. Special Research Committee has been published.[34] The general programme for experimental work and publications recently formulated is outlined, and the work already accomplished is summarised briefly. Particular attention has been given to the co-ordination of data obtained by various investigators on viscosity under high pressure, to the study of pressure distribution in the oil film as applied to both thrust bearings and journal bearings, and to the development of methods for measuring oiliness. Experiments indicate that the ordinary laws of viscosity may safely be relied upon down to a film thickness of 0·000001 in.

The apparent simplicity of estimating acidity in oils is being seriously challenged, especially with used oils, mainly because of the doubtful end point when using phenolphthalein. A popular utility or universal indicator has been examined by McCrumb.[35] He has shown that errors as high as 30 per cent. may be committed by using an indicator the pH of which is far removed from that of the solution and test. The so-called universal indicators cover a wide pH range and can be used with safety only on well buffered solutions. Unfortunately in testing unknown solutions there is no simple way of determining the buffer capacity and consequently pH control, under such circumstances, becomes somewhat uncertain.

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[31] *Petr. Z.*, 1931, **27**, 41; *J.I.P.T.*, 1931, **17**, 179 A.
[32] *Brenn.-Chem.*, 1930, **12**, 25; *J.I.P.T.*, 1931, **17**, 187 A.
[33] *Petr. Z.*, 1931, **27**, *Motorenbetreib*, **7**, 3.
[34] *Trans. Am. Soc. Mech. Eng.*, 1931, **53**, 21.
[35] *Ind. Eng. Chem. Anal.*, 1931, **3**, 233.

Investigators have turned their attention to the potentiometric methods, which may be criticised because they are long and tedious. Although no satisfactory method has established itself, there are definite indications that it will ultimately become the standard method.

Evans and Devonport[36] used the Ag-AgCl electrode. Clark, Wooten and Compton[37] utilise a valve amplifier. The electrode is a saturated calomel half-cell which is connected by means of an agar-agar-salt bridge. The titration is carried out in an atmosphere of nitrogen in the usual way.

To evade the difficulties of determining viscosity at a low temperature, Bulkley and Bitner[38] use a consistometer, and measure the rate of flow through a capillary under the pressure of mercury. Only 0·5 ml. of oil is required.

Downie Smith[39], in discussing the thermal conductivity of liquids, quotes the following results for a red oil :—30° C., 0·000337 ; 75° C., 0·000335 ; 100° C., 0·000329 ; and for light heat transfer oil, 30° C., 0·000316 ; 75° C., 0·000312 ; 100° C., 0·000309. Experiments were carried out by Kirkbride and McCabe[40] with water, light oil and heavy fuel oil, in determining the heat transfer to liquids in viscous flow.

Schultz[41] has calculated the latent heats of vaporisation of normal paraffin hydrocarbons utilising their specific heats.

The determination of mean molecular weights of lubricating oils by improved cryoscopic methods has been undertaken by Gullick.[42] His results on several oils lie between 315 and 737.

Zhuze[43] gives the thermal conductivity in cal./cm./sec./degree of spindle oil (d_{15} 0·8642) ; 20° C., 0·367 ; 30° C., 0·428 ; 110° C., 0·630 ; transformer oil 30° C., 0·390 ; 50° C., 0·440 ; cylinder oil (d_{15} 0·9233) 20° C., 0·308 ; 50° C., 0·350 ; 110° C., 0·438.

Kyropoulos[44], continuing his work on the physical properties of lubricants, has devised a method for determining to which group of substances a given compound belongs. By this method Penna oils have been identified as isoparaffin mixtures. The method is based on diagrams showing the relationship between molecular weights and *ns* for homologous series of the paraffins. The question has often arisen whether paraffins, resins and asphalt

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[36] *Ind. Eng. Chem. Anal.*, 1931, **3**, 82.
[37] *Ind. Eng. Chem. Anal.*, 1931, **3**, 321.
[38] *Bur. Stand. J. Res.*, 1930, **5**, 83.
[39] *Ind. Eng. Chem.*, 1930, **22**, 1246.
[40] *Ind. Eng. Chem.*, 1931, **23**, 625.
[41] *Ind. Eng. Chem.*, 1930, **22**, 785.
[42] *J.I.P.T.*, 1931, **17**, 541.
[43] *Azer. Neft. Khoz.*, 1929, 8-9, 70.
[44] *Z. physik. Chem., Abt. A.*, 1929, 144, 22.

are present in colloidal or in true solution. Zaharia and Lucatu[45] using an ultrafilter containing vulcanised rubber membranes found that resins separable by 70 per cent. ethyl alcohol were unfilterable, likewise was the paraffin in the petroleums used, but both the hard and soft asphalt were quantitatively removed by ultrafiltration. Hence the asphalt is colloidal but the paraffins and resins are not.

Shaw[46] states that tribo-electricity and friction are two aspects of the same phenomenon. In all cases of solid contact solid combination takes place on contact. The law of friction is limited in application and becomes invalid for extreme surface curvatures as well as extreme loading. Shaw and Leavey[47] also state that the coefficient of friction must be defined in terms of the history and physical conditions of the reacting surfaces. Charts prepared by Griffiths[48] show the relationship of coefficient of friction to viscosity and to bearing pressure. Fink[49] may expect to receive a challenge to his suggestion that oxidation is an essential to wear. In an X-ray investigation, using the crystal rotation method applied to a drop of liquid, Trillat[50] has shown that fatty acids are oriented on the surface of water or glass, since the surface of the liquid has a crystal structure, while the interior of the liquid does not. The attraction of the acid radical for the surface of metals accounts for the lubricating qualities of the oil, inasmuch as the COOH group neutralises to a certain extent the intense electromagnetic field radiated from the metal, and thereby reduces friction.

A comprehensive survey of experimental research directed towards perfect oil-film lubrication is made by Illmer.[51]

As bearing metals and bearings are inseparable from lubrication, a comprehensive paper by Corse[52] deserves mention.

Progress in engine design is compelling us to view the subject from new angles. Mougey[53] reminds us that coefficient of friction is not a measure of the tendency to seize. Lard oil gives a much lower coefficient of friction than certain transmission lubricants, yet it permits the bearing to seize at 13,000 lb. pressure, while with the special lubricant seizure does not occur even at 25,000 lb.

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[45] *Bul. Soc. chim. Romania*, 1930, **12**, 90.
[46] *Phil. Mag.*, 1930, **7**, 628.
[47] *Phil. Mag.*, 1930, **7**, 809.
[48] *Power*, 1930, **72**, 791.
[49] *Trans. A. Soc. Steel Treating*, 1930, **18**, 204.
[50] *Metallwirtschaft*, 1930, **9**, 1023.
[51] *J.S.A.E.*, 1930, **26**, 67.
[52] *Trans. Am. Soc. Steel Treating*, 1930, **18**, 179.
[53] *Oil and Gas J.*, 27.3.30, **28** (45), 41, 147.

pressure. Another new aspect is revealed by King and Moss[54]. They have made tests to determine the deleterious effect of various mineral oils on the anti-knock properties of motor fuels. Larson[55] has made an attempt to classify transmission and rear-axle lubricants. With the introduction of the lead soap and sulphurised lubricants such a classification will be necessary.

New processes for the preparation of special lubricants, referred to by Steinitz[56], include the improved Voltol process which is applicable to mineral, vegetable and animal oils; the Continentale A.-G. für Chemie process of increasing the viscosity of fatty oils by heating under vacuum to 150–250° C. without blowing, and the Daimler process of adding "bridge hydrocarbons" composed of compounds belonging to the system $X\text{-}CH_2\text{-}Y$, where X represents an aromatic or aliphatic radical, and Y an aromatic radical. Champsaur[57] has joined the band which is endeavouring to re-establish a popularity for olive oil. The invention of Prendergast, Prendergast and Sonsthagen[58] relates to lubricants for use with parts of machinery subject to friction under conditions of rapidly varying local pressure. In such circumstances corrosion frequently occurs. The corrosion is caused by electrolytic action and may be prevented if the lubricant be rendered sufficiently anodic with respect to the part to be protected by addition of a suitable quantity of a metal or metallic oxide. In cases of steel ZnO is used. For glass stopcocks Boughton[59] applies an amalgam after silvering the surfaces, also he uses a lubricant made by dissolving 10 gr. HPO_3 in 100 ml. water, adding 2 gr. H_3BO_3 crystals, evaporating to 25 ml., add 1 ml. H_3PO_4. Heat to 122° C. Water soluble lubricant may be made from $NaPO_3$ and $Na_2B_4O_7$.

Consumption is of course of economic interest, but it is also important in engine efficiency. The influence of piston design on the consumption of oil in the internal combustion engine is considered by Dentilhac.[60] Boerlage[61] records interesting observations on engines developing gummy pistons when running for short periods on no-load.

Evaluation of lubricating oils by the work factor method by O'Neill and McGeary[62] is based on the behaviour of oils in actual

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[54] *Engineering*, 1931, **131**, 1.
[55] *J.S.A.E.*, 1931, **28**, 321.
[56] *Chem.-Z.*, 1930, **54**, 837.
[57] *Ann. des Comb. Liq.*, 1930, **5**, 987.
[58] E.P. 327,097, 1930.
[59] *J.A.C.S.*, 1930, **52**, 2421, 2813.
[60] *Rev. Petr.*, 1931 (415), 331.
[61] *J.I.P.T.*, 1930, **16**, 678.
[62] *Nat. Petr. News*, 11.6.30, **22** (24), 63.

operation. McKee[63] has presented in tabular form information from 68 large users of cutting oils.

The Federal Specifications Board[64] has submitted a proposed revision of specifications for Class D lubricating oil which involves a system of grading the oils numerically from a consideration of their main physical properties.

The decomposition of lubricating oils is so important to the user that one may expect to find many views expressed upon the subject. Unfortunately the literature still contains references to aspects of the subject which have long been discarded. Vellinger[65] has applied the spectroscope to watching the deterioration of an oil in service. If the values of I/I_0 for a definite wave length are plotted against the time of service, a straight line is obtained and the slope of this curve gives a measure of the rate of deterioration. Beer's law is found to apply to solutions of mineral oil in chloroform and to a mixture of two oils one of which is colourless. Damian and Dixmier[66] have measured the change in viscosity, saponification value, iodine value and average molecular weight after heating the oil in a special oven at certain intervals. It is claimed that 30 hours' test in the oven is equal to 150 hours in an engine.

An interesting review on carbonisation of lubricating oils has been compiled by Bassett.[67] Boisselet and Mouratoff[68] have investigated the various forms of oxidation ageing tests and the products formed in the test. A paper of interest to workers on the products of oxidation of lubricating oils is by Swan, Howard and Reid.[69] It is true that these workers were concerned with the identification of products of oxidation of gas oil by the Penniman process. According to Vellinger and Marchand[70] the nature of the solvent has a distinct influence on photolysis. Carbon tetrachloride, chloroform and amyl alcohol are the most active. No change takes place in acetone and ether. When paraffin wax is oxidised with air at 170° C. it gives saponification values of 88·8 and 147·4 after 2 and 4 hours respectively. If 1 per cent. of manganese soap is added before oxidation, the corresponding values are 97·2 and 169·5, whilst if 1 per cent. of manganese soap be added, associated with 0·1 per cent. hexamethylene tetramine,

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[63] *Machine Shop Practise*, 1930, **52**, 13, 103.
[64] *Oil and Gas J.*, 8.1.31, **29** (34), 122, 127.
[65] *Ann. des. Comb. Liq.*, 1930, **5**, 273.
[66] *Chem. et Ind.*, 1930, **23**, 834.
[67] *Chem. & Ind.*, 1931, **9**, 527.
[68] *Chim. et Ind.*, 1931, *10th Cong. Chim. Ind.*
[69] *Ind. Eng. Chem.*, 1931, **23**, 1277.
[70] *Ann. des. Comb. Liq.*, 1930, **5**, 977.

the saponification values amount to 135·5 and 217 respectively, and after 6 hours to 271·2. Hence oxidation is accelerated when metallic catalysts are associated with organic nitrogen bases.

The activity which was so evident during the past few years in the realm of anti-oxidants has waned somewhat since it has been found that many of them increase the rate of oxidation after a period of usefulness when used in an engine. Lederer and Zublin[71] ask whether doped oils stand up to practical conditions. To the very long list of anti-oxidants Kaegebehn[72] has added 4-hydroxybiphenyl.

During the past two years much time has been absorbed in criticising the various oxidation and ageing tests, and defending the existing methods. This has been inevitable through the effort to formulate an International Standard method. When the various reports are published they will afford interesting reading. They will probably show that the Michie Sludge Test, which has many supporters in England, is in many respects superior to methods which are recommended in other countries. Various methods of testing insulating and turbine oils are discussed by Evers and Smidt.[73] They have developed a new method whereby electrolytic oxygen is absorbed at 100° C. by a measured amount of oil distributed over silica gel impregnated with Fe_2O_3 as catalyst. The amount of oxygen absorbed is determined at intervals by measuring the current passing through the electrolytic cell. With the aid of the spectroscope Vellinger[74] has found that mineral oils do not show any definite absorption bands in the visible spectrum, but in the region of low wave length the absorption rises rapidly. This rise commences from $\lambda=450$ for a yellow oil to $\lambda=600$ for a dark oil. If the values of $1/1°$ for a definite wave length are plotted against the time of service a straight line is obtained, and the slope of this curve gives a measure of the rate of deterioration. To the few who still take an interest in the sulphuric acid absorption a paper by Toennies[75] will be of interest.

The German Association for Testing Materials have published test methods.[76] Sir William Hardy has made another very valuable and lengthy contribution to the subject under the title of Analysis of Commercial Lubricating Oils by Physical Methods.[77] Experiments in the field of boundary lubrication with two lubricating

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[71] *Nat. Petr. News*, 13.8.30, **22** (33), 63.
[72] U.S.P. 1,784,359, 1930.
[73] *Brenn.-Chem.*, 1930, **11**, 214.
[74] *Ann. des. Comb. Liq.*, 1930, **5**, 273.
[75] *Petr. Z.*, 1931, **27**, 527.
[76] *Petr. Z.*, 1930, 26, *Motorenbetrieb*, 5, 3-9; 6, 9-14.
[77] Dept. Sci. Ind. Research, Lub. Research, *Tech. Paper No.* 1, 1930.

oils indicate that it is possible to obtain all the necessary information concerning an unknown oil from two temperature curves taken respectively in air and nitrogen. A commercial lubricating oil consists of a diluent and a number of components which may form only a small percentage of the oil.

In 1929 the I.P.T. discarded the pour point in favour of a setting point, but complete satisfaction does not appear to have been attained. The modern tendency points to an abandonment of this type of test, and developing one based on the measurement of viscosity at low temperatures. Terpugoff[78] states that deviations between the observed and calculated setting points of mixtures may be positive or negative according to the constituent oils. In some cases the setting point of the mixture is lower than the setting point of the initial oils. This is of peculiar interest at the moment owing to the recent introduction of the oil Paraflow, which is claimed to have the power of reducing the pour point of other oils.[79] The Ubbelohde apparatus for the determination of the drop point for petrolatums is now being used by a number of chemists to determine the melting point of greases. It appears to be reasonably accurate for lime soap greases, but it is not so satisfactory for soda soap greases. Values may differ according to Schwarz[80] by 25° C. due to differences in diameter or length of the glass tubing, and to the depth to which the thermometer bulb is immersed. Rate of heating, and moisture in high-temperature lubricants also influence the results. Der Deutscher Normenausschuss have standardised the apparatus, but as the glass tubes are difficult to make they should be calibrated before use. The relationship of wax content to cloud point and pour point is discussed by Japour.[81]

In view of the interest which is now being taken in the high vacuum distillation of lubricating oils, a paper by Gavin and Foster[82] describing an apparatus for vacuum distillation of lubricating oils is of interest. Also a paper by Vellinger and Orlovski.[83] They state that the refining of an oil lowers the dispersion of the refractive index in the visible spectrum. Samples of various oils were subjected to distillation in a cathodic vacuum, and the n_{578}, n_{546} and n_{435} of the fractions determined at 19°. The products coming over at the same temperature do not always have the same constants, probably because of entrainment of

[78] *Petr. Z.*, 1929, **25**, 1213.
[79] Davis and Blackwood, *Ind. Eng. Chem.*, 1931, **23**, 1452.
[80] *Seifensieder Ztg.*, 1930, **57**, 877.
[81] *Petr. Eng.*, 1930, **1** (8), 121.
[82] *Nat. Petr. News*, 21.5.30, **22** (21), 83.
[83] *Ann. des Comb. Liq.*, 1930, **5**, 959.

heavy products. Esau[84] proposes a method to test the purity of solid and liquid hydrocarbons in which the material to be tested is subjected to the action of short electric waves (10^8 Hertz), and the resultant changes of temperature therein are measured. A particular application of the invention is the determination of the water content of insulating oils. Kremer[85] quotes Hesle's method which can be applied to determine quantities of water as small as 0·05 per cent. The method is based on the formation of anhydrous conversion products, *e.g.*, $Al_2(O{\cdot}C_2H_5)_4O$ and $Al_4(O{\cdot}C_2H_5)_6O_3$ obtained from normal aluminium ethylate. These compounds when dissolved in xylene give a voluminous precipitate of aluminium hydroxide when traces of water are present. Wiegand, Boggs and Kitchin[86] refer to the ability of carbon black (Micronex) to remove water, and Boyer[87] suggest the use of two to three parts of oxycellulose to 1000 parts of oil. The B.D.V. of the treated oil is 45,000 volts.

Pacheco[88] helps to clarify some of the difficulties incurred in determining sulphur in heavy oils by the A.S.T.M. lamp method.

Parker[89] gives some useful hints on the measurement and sampling of mineral oil, and Nothnagel[90] renews our interest in the capacity of the barrel.

Cold-starting characteristics of automobiles is very closely linked with lubricating oil. Blackwood and Rickles[91] found that a particular car engine having a cranking speed of 21½ r.p.m. when using an oil having a viscosity of 50,000 seconds (Saybolt) at the starting temperature of 10° F. would start. Working at the same temperature and using an oil of 60,000 seconds viscosity, and cranking speed of 16½, the engine would not start. The exact viscosity and cranking speed which would just produce a start is determined by plotting all the data for all the tests made on each car and locating the limiting point on the curve. This point must vary enormously with different cars. No relation exists between size of engine or number of cylinders to ease of starting. Kent[92] has enlarged upon the subject, but more from the engineer's aspect.

Over anxiety to solve the starting difficulty by using a thin oil plunges one into the oil consumption problem. Oil consumption

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[84] E.P. 345,464, 1931.
[85] *Petr. Z.*, 1931, **27**, 443.
[86] *Ind. Eng. Chem.*, 1931, **23**, 273.
[87] U.S.P. 1,760,539, 1930.
[88] *Chemist Analyst*, 1931, **20** (1), 10-11.
[89] *J.I.P.T.*, 1930, **16**, 565.
[90] *J.I.P.T.*, 1930, **16**, 576.
[91] *J.S.A.E.*, 1931, **28**, 234-239.
[92] *J.S.A.E.*, 1931, **29**, 141-147.

as affected by engine characteristics has been analysed by Mougey[93]. He places the factors affecting oil consumption under eight headings in order of importance : engine speed, oil leaks, design and wear, viscosity, volatility, pour test, carbonisation, length of time between oil changes. The oil consumption on a test car fell from 1200 miles per gallon when run at 20 m.p.h. to 100 miles per gallon when run at 70 miles per hour. Considerably higher consumption is experienced when using a thin oil than when using a thicker oil.

It is generally supposed that the major portion of the oil which passes the top ring is burned. Minter and Finn[94], by using hydrogen instead of gasoline in an engine, find that only a negligible amount of oil is burned.

A thin oil is desirable for easy starting, but if the engine runs hot a high viscosity oil is necessary to maintain a film at high temperatures. Oil cooling and oil coolers have therefore to be considered. Ramsaur[95] gives a series of charts dealing with strength of bearing metals and viscosities of oils at various temperatures. He quotes the case of a car having run 200 miles at 80 miles per hour with a cooler with maximum oil temperature of 215° F. With cooler removed the oil reached 275° F. in 50 miles, when the bearings failed. Heat dissipation is a live problem to-day.

Motor oil consumption increases six or seven times when car speeds jump from 30 to 55 miles per hour. The modern tendency towards driving at high speed is the main factor causing variation in oil consumption.

The introduction of the hypoid gear, and the increase of horse power transmitted to the rear axle, has demanded lubricants superior to the well-established mineral oil type. Even castor oil, which is favoured for worm drives, has not proved sufficiently satisfactory for the new conditions. To meet these conditions the lead soap lubricants have gained a popularity. Although they have been known and used for several years, their true values have only recently been recognised. The writer used a mixture of lead stearate and filtered cylinder oil in 1917, but it was not until 1930 that the real demand for this class of lubricant arrived.

At first simple mixtures of lead soap and petroleum products were used, subsequently mixtures containing tar products appeared, and then came the so-called sulphurised oils. Most of the lead soap lubricants have entered the market as proprietary articles,

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[93] *J.S.A.E.*, 1931, **29**, 200-214.
[94] *Ind. Eng. Chem.*, 1931, **23**, 285.
[95] *J.S.A.E.*, 1931, **28**, 4, 429-437.

consequently their compositions have not been revealed. Whatever their composition may be, it cannot be denied that they occupy a transitional phase, nor can it be concealed that the design of heavy road vehicles is momentarily arrested by the demand for more and more effective rear axle lubricants.

Edwards[96] has discussed lead soap lubricants and their use. As no satisfactory explanation of their film-forming tendency is available, any discussion on them is handicapped. However, observations on the testing of lubricants by Wooler[97] throw some practical points out into relief. He reminds us that on American cars the tooth pressure has risen from 925 lb. in 1924 to over 1800 lb. per sq. in. in 1930, and that scored teeth were a common experience. He designed a machine to determine the load carrying capacity of lubricants for spiral bevel and hypoid gears. With this apparatus he demonstrated the advantage of adding lead oleate to a mineral oil. His adverse criticism is that the instability of these lubricants leads to excessive wear. During 1931 considerable progress has been made to prevent separation.

Larson[98] has made an attempt at classifying transmission and rear axle lubricants.

Otto[99] discusses the manufacture of lead containing lubricants.

The present position is that lead soap lubricants are proved products, provided no lead oxide is in suspension to act as an abrasive. The introduction of sulphur has led to complications demanding more study.

The pour point of a gear lubricant is of little value in determining whether the lubricant will feed satisfactorily at low temperatures. True indications can only be determined by measuring viscosity under pressure, and comparing the results with those obtained in the device for making transmission gearshift test. The results on these tests of a wide range of lubricants are tabulated with film strength tests and high temperature performance. Larson indicated that 1,500,000 seconds (Saybolt) is about the maximum viscosity at which to shift gears.

This subject cannot be closed without a word upon reclaiming, or as Herschel[100] prefers to call it, re-refining crankcase oil. The drainings from crankcases of motor vehicles are difficult to dispose of. In some places they can be used in the war against mosquitoes, or mixed with fuel oil as fuel. The new oil when in use becomes

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[96] *J.S.A.E.*, 1931, **28**, 50-52.
[97] *J.S.A.E.*, 1931, **28**, 53-65.
[98] *J.S.A.E.*, 1931, **28**, 321-331.
[99] *Petr. Eng.*, 1931, **2** (10), 75; *J.I.P.T.*, 1931, **17**, 400 A.
[100] *J.S.A.E.*, 1930, **27**, 671-678.

contaminated with petrol, road dust, solid oxidation products, acids, etc. The solids can be removed by the centrifuge, the petrol by dry or steam distillation, and the colour partially restored by treatment with one of the usual filtration earths. Whether the treatment is of economic value must depend upon a number of factors, not the least of which is whether the resultant oil is sufficiently good for reuse.

Clark and Harding[101] have patented the use of tricresyl phosphate for extracting the impurities, and the removal of the solvent by addition of acetic acid. They advocate the automatic purification of transformer oil during use by the addition of tricresyl phosphate to the unused oil. As oxidation proceeds the ester becomes insoluble and separates, carrying with it the dissolved oxidation products. The British Thomson-Houston Co.[102] have patented an allied idea. A charge of glycerol or other equivalent polyhydric alcohol is maintained in contact with the oil, but out of contact with the insulation and electrical members. It appears to function as a neutral solvent extracting impurities formed in the oil during use.

[101] U.S.P. 1,798,968, 1931; *J.I.P.T.*, 1931, **17**, 272 A.
[102] E.P. 345,708, 1931; *J.I.P.T.*, 1931, **17**, 318 A.

Gas Oils, Diesel Fuels and Fuel Oils.

By F. H. Garner, Ph.D., M.Sc., F.I.C. (Member).

During the past two years much attention has been devoted to the various questions connected with Diesel engine fuels, and a marked impetus in England has been given to the use of the heavier type of fuels in road transport by the increase in price of gasoline due to increased taxation.

Special attention has been also given to the evaluation of gas oil by physical and chemical methods as an alternative to small plant scale tests.

Gas Oils.

The desirable tests for determining the quality of petroleum wash oil for the removal of light oils from coke-oven gas are considered by H. R. Mathias[1]. He points out that deposits formed in scrubbing towers are due primarily to coal derivatives held in the oil which have been altered by oxidation and polymerisation. Olefines are not responsible for sludging, which can be eliminated by maintaining specific gravity, viscosity, and emulsion test as low as possible. High distillation losses are due to the use of oils of too low initial boiling point, and Mathias considers that an oxidation sludge test will give more accurate results for estimating the relative stability of absorbent oils in use than inferences drawn from olefine content.

The physical characteristics necessary for absorbent oils in natural gasoline recovery are given in an article by F. L. Kallem[2], who concludes that molecular weight should be of the order of 150–200. Other tests which are considered necessary are the average boiling point, demulsibility factor, freedom from wax separation at the lowest operating temperature, in addition to the viscosity of the oil.

A study of gas oil operation for the production of carburetted water gas is described in the Proceedings of the American Gas Association for 1930, page 1423, in which a small laboratory apparatus was used for investigation of variation in the rate and method of oil introduction. The introduction of the oil as a spray with the blue gas under high pressure was found to show the following results in comparison with the ordinary method :

Decrease of 21 per cent. in oil gas production per gallon of oil used was combined with slightly increased thermal value of the finished gas, and decrease in oil forming carbon.

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[1] *Ind. Eng. Chem.*, 1931, **23**, 804.
[2] *Chem. and Met. Eng.*, 1931, **38**, 78.

The first report of the Back Run process for the manufacture of carburetted water gas[3] has been issued by the Institution of Gas Engineers, and in a further report the unsatisfactory results by the use of light and heavy creosote as compared with gas oil are noted.[4]

A method for the evaluation of gas oils by laboratory cracking method has been described by E. J. Murphy.[5] A measured quantity of gas oil is fed from a burette into a cracking tube which is automatically heated to maintain a constant temperature. Measured amounts of water to form steam and of blue gas are also passed through the tube. Tar is removed by condensers, and it is claimed that reproducible results are obtained with this form of apparatus.

During the last two years, considerable attention has been paid to the evaluation of gas oils by chemical means, but up to the present time, no generally acceptable method has apparently been obtained.

In a report of the Sub-committee on the Evaluation of Gas Oils issued by the American Gas Association, a comparison is made of Griffiths' and Mighill's methods. Both of these methods determine the concentration of the various types of hydrocarbons—paraffin, naphthene, aromatic, and unsaturated—present in gas oils by what are admittedly empirical methods, and definite values are ascribed to the different types of hydrocarbons. A brief description of the basis of these two methods was given in the report on progress of naphthology of this Institution for 1930. A new suggestion was put forward, dependent upon the separation of gas oils into two groups, unsaturated and aromatic on the one hand, and the so-called naphthene and paraffin on the other hand. The separation is made by the use of two concentrations of sulphuric acid as in Griffiths' method, and the results are reported as "absorbables" and "residue." The efficiency of the absorbables is given as 50 per cent. and the residue as 80 per cent.

Experimental results are quoted on the use of two products, one a low melting point, specially purified paraffin wax, and the other a refined oil of about 315° C. final boiling point, consisting of nearly 77 per cent. naphthenes as determined by the Griffiths method. For each temperature, suitable conditions were maintained to secure the highest B.Th.U.'s per gallon of oil imparted to the gas, and the general conditions approximated what is found in good generator practice. The results indicate the naphthenes to be of high carburetting value, which is contrary to the assumptions made in previous methods of evaluation. Comment is also

[3] *Gas J.*, 1930, **192**, 704.
[4] *Gas J.*, 1930, **192**, 703.
[5] *Gas Age Record*, 1930, **65**, 389, 395.

made in this report on the evaluation of gas oils by the use of small scale laboratory apparatus, but no definite recommendation is put forward.

The use of heavy oils for carburetting is described by P. T. Dashiell,[6] the method being either that of spraying on empty carburetter walls or that of blasting the upper portions of the generator fire and distributing the oil on the fire top.

In a paper dealing with methods of prevention of trouble due to the formation of naphthalene in gas service mains[7] a comparison is given of the use of scrubbers using absorbent oils, such as gas oil and anthracene oil, with the results obtained by injection of liquids such as tetralin or kerosine into the gas. Scrubbers are superior to vaporised solvents owing to their ability to remove gums, and are also cheaper if the gas oil is reclaimed and used in a water gas plant. The effect of unsaturated hydrocarbons in the production of deposits in meter leathers and moving parts is described by R. S. Andrews.[8] The unsaturated hydrocarbons present in the light oil content of carburreted water gas are the result of imperfect cracking due to the use of too low temperatures in the carburetters. The importance of other factors, such as low oxygen content of the gas, is also discussed. It is claimed that gas from horizontal retorts is likely to be less damaging to the meters than gas from vertical retorts.

Diesel Fuel Oils.

At the World Power Conference in Berlin 1930,[9] J. Kewley gave a survey of the economic aspects of the future supplies of Diesel fuel oil in connection with the development of the Diesel engine. He points out that extension of the use of Diesel engines will result in competition for distillates with an inevitable increase in price in comparison with gasoline. The development of engines capable of running on residual fuels presents the line of development most clearly indicated, since these fuels may be expected for years to come to be the cheapest petroleum product.

Considerable attention has been paid to the mechanism of the atomisation of Diesel fuels, and an account of the work carried out in America will be found in papers by R. A. Castleman[10] and in publications of the National Advisory Committee of Aeronautics.[11]

[6] Ibid., 1931, **67**, 223.
[7] *Het Gas*, 1931, **51**, 246.
[8] *Gas J.*, 1931, **193**, 158, 212.
[9] *Trans. 2nd World Power Conference*, 1930, **8**, 43.
[10] *Bur. Stand. J. Res.*, 1931, **6**, 369.
[11] *National Advisory Committee for Aeronautics* (*U.S.A.*), 1931, *in Aircraft Eng.*, 1931, **3**, 281.

A number of authors have called attention to the desirable qualities in Diesel engine fuels, and reference may be made to the paper read by W. H. Graves, of the Packard Corporation, to the American Petroleum Institute in 1930 on airship Diesel engine fuels. The question of fuel flow is considered one of the most important requirements for this purpose, and he has found a pour point of —30° F. to —50° F. to be satisfactory for general commercial work. Under special circumstances fuel of —80° F. pour point is necessary. No trouble has apparently been experienced with different grades of fuel commercially obtainable as far as ignition is concerned, although it is stated that the oils used have had spontaneous ignition temperature of about 500° F. by the A.S.T.M. method. The calorific value is naturally of great importance, but whilst distillate fuel oil is essential because of its freedom from residual matter, the distillation range is considered of minor importance.

In a paper presented before the Institution of Automobile Engineers, G. J. Shave[12] gives an account of experimental work carried out by the London General Omnibus Company, and gives a general specification of fuel suitable for the present types of high-speed Diesel engines, in which the viscosity (Redwood No. 1) at 100° F. is given the range of 35–70 in., while a maximum sulphur content of 2 per cent. is allowed. He points out that coal tars are definitely less suitable for Diesel engines than are petroleum and shale oils, and in addition the creosotes and anthracene oils, on account of their content of oxygenated compounds, have relatively low calorific value, resulting in inevitable increase in fuel consumption. Goddard[13] gives a general description of the requirements of fuel oil for Diesel engines used in road transport.

A number of important papers dealing with mechanism of combustion and the rating of fuel oils as regards their behaviour in Diesel engines have appeared. Ricardo[14] makes a parallel between combustion in gasoline and Diesel engines, and points out that in both there is a delay period occupied by the building up of a substantial nucleus of flame followed by a rapid pressure rise. In the Diesel engine there follows a third stage in which the fuel burns as it enters from the injection nozzle. All these three phases are shown on indicator diagrams given in the paper. Reference should also be made to the very interesting lectures given by Ricardo to the Royal Society of Arts (Howard Lectures).

In a paper by S. J. Davies and E. Giffen[15] an interesting summary is given of the work of Hawkes, Bird, and Newman on the

[12] *Proc. Inst. Aut. Eng.*, 1930–31, **25**, 93.
[13] Ibid., 1929–30, **24**, 237.
[14] Ibid., 1929–30, **24**, 645.
[15] Ibid., 1930–31, **25**, 399.

phenomena associated with ignition lag or the delay period after the injection of the Diesel fuel in Diesel engines. Reference is made in this paper to the effect of ethyl nitrate on the reduction of ignition lag, and curves are shown illustrating the effect of the addition of 5 per cent. of ethyl nitrate, giving a much smoother indicator diagram than with the undoped fuel.

W. Helmore[16] has described a non-volatile fuel to which are added two primers, one of which has a lower spontaneous ignition temperature than the fuel oil itself (*e.g.*, methyl nitrate), and at least one of which explodes when rapidly heated (*e.g.*, ethyl nitrate). The latter ingredient may have a higher spontaneous ignition temperature than the fuel oil. The exploding primer is dissolved in the igniting primer and the addition to the fuel oil is made as a solution in fuel oil.

Ormandy,[17] in the course of his paper on the fuel situation, in drawing attention to the importance of low spontaneous ignition temperature for Diesel engines, has pointed out the need for discovery of some substance having opposite properties to tetraethyl lead, namely, one which, in traces, would reduce the spontaneous ignition temperature of aromatic or phenolic oils and render them more suitable for high-speed Diesel work. He states that a very large number of products have been tested in his laboratory, but so far nothing superior to nitrobenzole and amyl nitrate have been found, and that no relationship has been discovered which would lead one to suppose that success might be attained by working along any definite line.

In an interesting paper presented before the American Society of Automotive Engineers, W. H. Butler[18] points out the different type of fuel required by the automobile Diesel engine as compared with that suitable for large, slow-speed engines.

Le Mesurier and Stansfield[19] give an interesting description of fuel testing in slow and high-speed Diesel engines. The physical and chemical tests of a wide range of fuels are described and four different types of engine were employed in this investigation, covering the examination of fuel combustion, ease of starting, effect of dope, and processes of combustion. They put forward a method for the evaluation of fuels based on indicator diagrams obtained with a "Farnboro" indicator. The relationship between the delay angle from the moment of lift of the spray valve and the beginning of pressure rise for each fuel is plotted against the injection timing. It is shown that each fuel has its own characteristics as regards delay

[16] E.P. 354,398.
[17] *J. Inst. Fuel.* 1931, **5**, 56.
[18] *Diesel Power*, 1931, **9**, 456.
[19] *J.I.P.T.*, 1931, **17**, 387.

angle for the different cylinder pressures, and therefore temperatures, at the moment of injection. The general results show that heavy oils obtained from crudes giving motor spirit of the highest anti-knock value are worst from the point of view of combustion shock in a Diesel engine, and those of crudes giving straight-run spirits of low anti-knock value will be comparatively good.

Work on the relationship of vapour pressure to the preparation of fuel for combustion in fuel injection engines has been discussed in a report of the National Advisory Committee for Aeronautics, U.S.A.[20]

The data for vapour pressures of fuels at high temperatures are an indication of compression pressures required to produce rapid vaporisation of the fuel for combustion, and it was shown in the case of a Diesel engine fuel oil that above 800° F. (425° C.), the vapour pressure increased at such a rapid rate that a comparatively small change in the temperature and consequently in the compression ratio of an engine will result in a considerable increase in the lag of auto ignition.

In a series of recent papers in *Engineering* by Boerlage and Broeze[21] a study is given of the ignition qualities of fuels in compression-ignition engines. A method of rating fuels in terms of the difference in delay measured at two given pressures is described. By tabulating the differences in delay between the two pressures as found for different fuels a comparison of the relative ignition quality of these fuels is obtained which can be checked against corresponding figures for standard fuels. A special 20 h.p. Thomassen engine was used for this purpose, with the aid of an optical indicator, a special gas oil and a coal tar oil being used as standard fuels. These authors also stress the importance of building engines to use the wide range of normal fuels available, rather than confining the fuels to the relatively few of highest ignition quality.

Two reports have been issued by the American Society of Mechanical Engineers Special Committee on Diesel fuel oil specifications, describing the results of some tests by the industry on sample Diesel fuel oils.[22] As as result of these tests, the importance of proper fluidity was emphasised, and it was shown that, when this is obtained by preheating, a much heavier fuel can be used. The viscosity of the oil at the pumps should be about 130 Saybolt Universal (115 seconds Redwood), dependent to some extent on the engine. It is pointed out that in mechanical oil burning, 50-130 Saybolt Universal (45-115 seconds Redwood) has been found satisfactory, and a similar range will probably meet the Diesel engine requirements, but further work is necessary.

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[20] W. F. Joachim and A. M. Rothrock, Report N.A.C.A., 321.
[21] *Engineering*, 1931, **132**, 603, 687, 755.
[22] *Trans. Am. Soc. Mech. Eng.*, O.G.P., 52–7, 52–8.

The work of this committee has now been extended[23] and sub-committees are studying three distinct projects: (1) Study of combustion and spray research from theoritical and laboratory angle; (2) Study of physical and chemical properties of Diesel fuels in laboratories of oil companies; (3) carrying out field tests in the shops of various engine manufacturers.

It is considered probable that the analysis of research results will have an even more important bearing on the problem of high-speed engine design than on the preparation of oil-fuel specifications—the primary object of this committee.

The American Society for Testing Materials, Sub-committee 28, has issued a report on the autogenous ignition of petroleum products, and has issued a revised version of its methods of test.[24]

Fuel Oils.

Industrial Uses.—In a paper by I. Lubbock[25] mention is made of the application of fuel oils to a large number of industrial processes with particular reference to the glass, ceramic, metallurgical and cement industries, and the use of fuel oil for central heating and the advantages of this type of fuel. Specifications of fuel oil for domestic burners, central heating, are given in *Oil & Gas Journal*,[26] stating limits for flash point, colour, cold test, and viscosity for five grades of oil. In some cases, points in the distillation range are also specified.

The Annual Survey of Fuel Oil Distribution for 1930 for the United States is given in a recent report of the American Petroleum Institute, December 1931. It is noteworthy that a marked increase in the use of oil for the heating of buildings has taken place, the expansion from 1923 to 1930 being nine times, and at the present time this particular use has become one of the major items of fuel oil demand. On the whole, however, nearly every industry, owing to unfavourable economic conditions, used less fuel oil in 1930 than in the previous year.

In a survey of the fuel consumption at petroleum refineries in 1930, the United States Bureau of Mines Report of Investigations No. 3145 shows a marked decline in fuel consumption in comparison with the throughput. Factors which have reduced fuel consumption are the introduction of pipe stills instead of shell stills, more efficient heat exchange, and improvements in furnace design. Modern furnaces are designed to utilise as much radiant heat as possible in contrast to the earlier days when it was thought that all heat should be transferred by convection.

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[23] *Mech. Eng.*, 1931, **53**, 909.
[24] *Proc. A.S.T.M.*, Pt. I, 1930, **30**, 788.
[25] *J. Inst. Fuel*, 1930, **4**, 90.
[26] *Oil and Gas J.*, 1931, **30** (14), 97.

Oil Engines.

By P. N. Everett, A.M.Inst.C.E.

Development has continued mainly along the lines indicated by the last review, and although the industry as a whole has suffered from the general depression in trade, there has, nevertheless, been several marked achievements.

The scarcity of orders and consequent keen competition has driven manufacturers to develop along the lines which will produce the engine of the least size, weight and cost. These lines are substitution of airless for air injection, super-charging on single-acting 4-stroke engines, the double-acting 2-stroke engine, and generally higher r.p.m., mean pressures, and piston speeds, with a greater number of smaller cylinders for multi-cylinder engines.

Improvements in metals have been readily used to this end, particularly for cylinder liners, pistons and bearings.

General improvements in detail have enabled the airless injection engine to give at least as good results as the air injection engine, when using a good fuel, but it is doubtful if the airless engine generally can yet use, with equally good results, as wide a range of fuels as the air injection engine.

Recent development is detailed under sections of application.

Stationary Engines.

The field for oil engines is extending both into the smaller powers and into the higher powers. Many firms are now supplying high compression heavy-oil engines of 5 B.H.P., while at the other end of the scale Burmeister & Wain are now building for a generating station an 8-cylinder, 2-stroke cycle, double-acting engine to develop 22,000 B.H.P. at 115 r.p.m., the cylinders being 840 mm. × 1500 mm.

During the past two years many engines of 5000, 6000 and 7000 B.H.P. have been put into service in various parts of the world, and there is little doubt that for peak loads of power stations oil engines are ideal.

For small and medium sizes, engines continue to be built as vertical and horizontal, 4- and 2-cycle, high and low compression, air and airless injection of the fuel, and those of the airless type, direct and prechamber, the exception being the 4-cycle low compression engine which has now disappeared entirely, and also very few air injection engines are now being built.

Probably the most popular type is the 4-stroke high compression engine using direct airless injection, a type of engine which is a British product, having originated in this country and been

developed here. The compression pressure is usually about 450 lbs. per square inch and the maximum combustion pressure about 650 lbs. per square inch. The fuel pressure is about 3000 lbs. per square inch. The fuel pump is usually of the constant stroke type regulated by a mechanically operated spill valve under governor control, and the sprayer of the spring-loaded type with a multihole nozzle. The engine is built in both single and multi-cylinder, and generally there is one fuel pump to each cylinder.

An interesting horizontal engine of this type has been developed by Robey's, Lincoln, which is totally enclosed and fitted with forced lubrication by a pump and hollow crankshaft similar to a modern vertical engine. This engine is made from 15 to 100 B.H.P. per cylinder in one to four cylinders. The 200 B.H.P. size runs at 220 r.p.m. and has two cylinders, each 15 ins. × 27 ins., and a fuel consumption at full load of 0·39 lb. per B.H.P. hour.

Probably the largest horizontal oil engine made was recently completed by the Premier Gas Engine Co., Sandiacre. This engine develops 1000 B.H.P. at 214 r.p.m. in 8 cylinders arranged *vis-a-vis* on 4 cranks, cylinders 18 ins. × 26 ins. The special feature of this type of engine is the design of the common crank pin bearing and the under running piston. The fuel consumption obtained on the official trial was 0·38 lb. per B.H.P. hour. This engine is also 4-cycle, high compression, and has direct airless injection. Three engines are on order for the Fenn Drainage Board.

A great deal of propaganda has been done for supercharging, but the application does not make the headway that the undoubted advantages would appear to deserve.

A recent notable installation is a Ruston Hornsby engine at the Ashford Power Station. This engine is a 6-cylinder, vertical, high compression, direct injection, 4-cycle engine, cylinders 18¼ ins. × 24 ins. The engine ran in Ruston's own Power Station as an unsupercharged unit and was rated at 850 B.H.P. at 250 r.p.m. Later, an exhaust gas turbine blower was fitted and the continuous rating raised to 1200 B.H.P. at 250 r.p.m., fuel consumption 0·376 lb. per B.H.P. hour.

Continental makers are pushing the vertical multi-cylinder engine, and to reduce the price are continually increasing the speed; such engines demand a better grade of fuel than the slow speed horizontal engines favoured by the English builders, and it is not at all certain that the development is good considering the number of oil engines used in undeveloped parts of the world. On the other hand, there is often an enormous saving in the cost of the machine to be driven when high speeds can be used, say, dynamo, pump or compressor. Some English builders are also developing along this line.

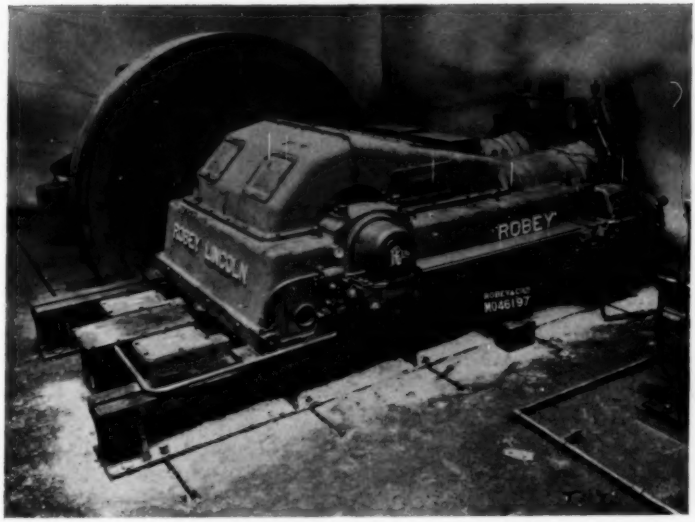

FIG. 1.

ROBEY 4-CYCLE, 2-CYLINDER, HIGH COMPRESSION OIL ENGINE. 200 B.H.P. AT 220 R.P.M.

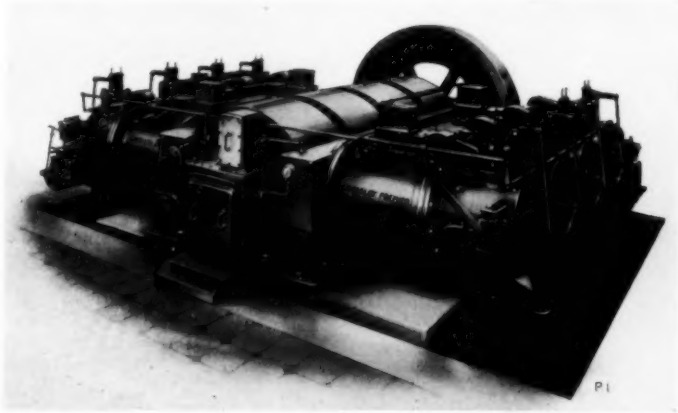

FIG. 2.

PREMIER VIS-A-VIS 8-CYLINDER OIL ENGINE. 1000 B.H.P. AT 214 R.P.M.

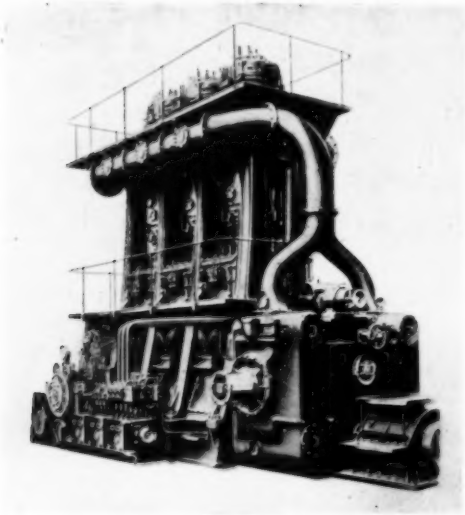

FIG. 3.

RICHARDSON WESTGARTH 2-CYCLE, DOUBLE-ACTING, MARINE OIL ENGINE FITTED IN M.V. "IRANIA."

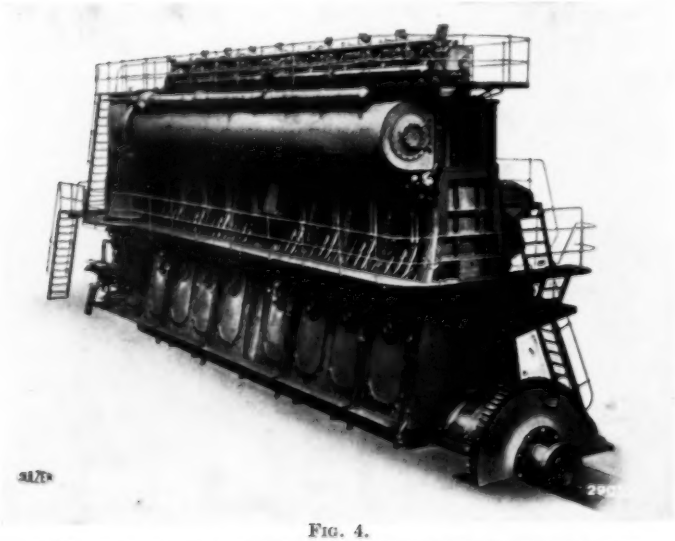

FIG. 4.

7600 B.H.P., DOUBLE-ACTING, SULZER 2-CYCLE DIESEL ENGINE FOR M.V. "TAJANDOEN."

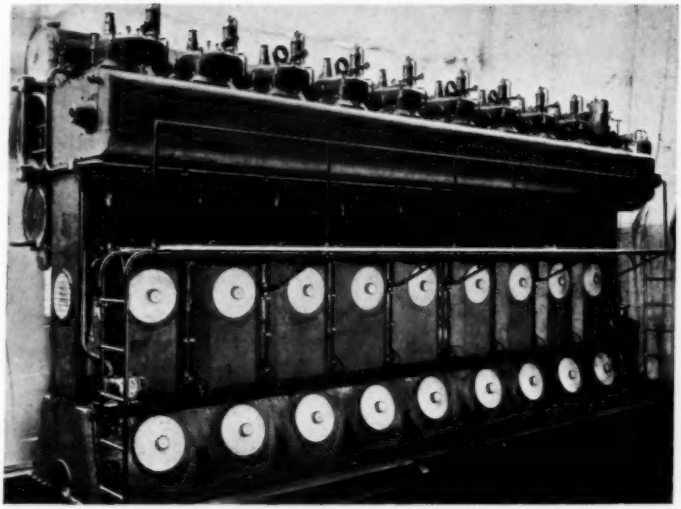

FIG. 5.

M.A.N. 2-CYCLE, DOUBLE-ACTING, MARINE OIL ENGINE. ONE OF THE EIGHT MAIN ENGINES OF THE "DEUTSCHLAND." 7100 B.H.P. AT 450 R.P.M.

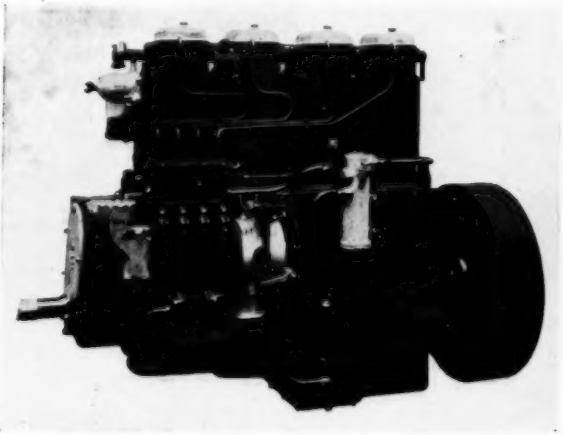

FIG. 6.

FOUR-CYLINDER GARDNER HIGH COMPRESSION MARINE ENGINE, 50 B.H.P. AT 1350 R.P.M.

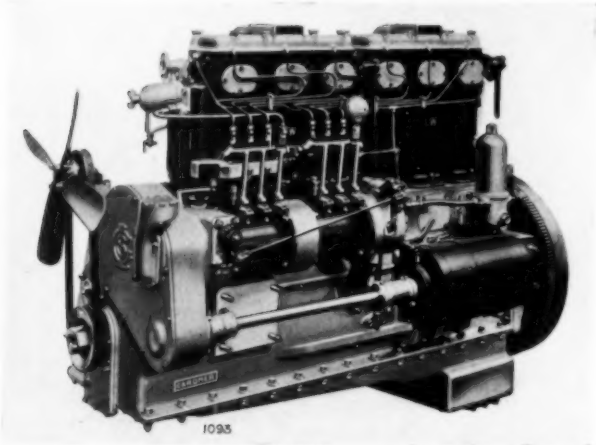

FIG. 7.

SIX-CYLINDER GARDNER HIGH COMPRESSION ENGINE AS FITTED TO LORRIES AND 'BUSES, 102 B.H.P. AT 1700 R.P.M.

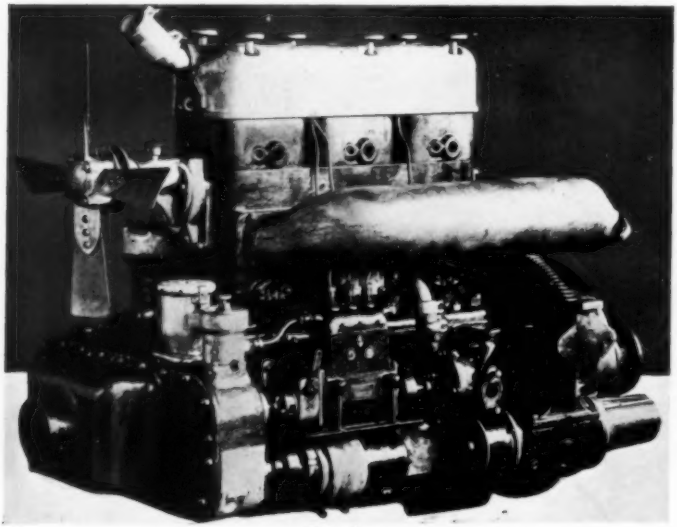

FIG. 8.

PETTER 3-CYLINDER, 2-CYCLE, HIGH COMPRESSION OIL ENGINE FOR ROAD VEHICLES. 36 B.H.P. AT 1200 R.P.M.

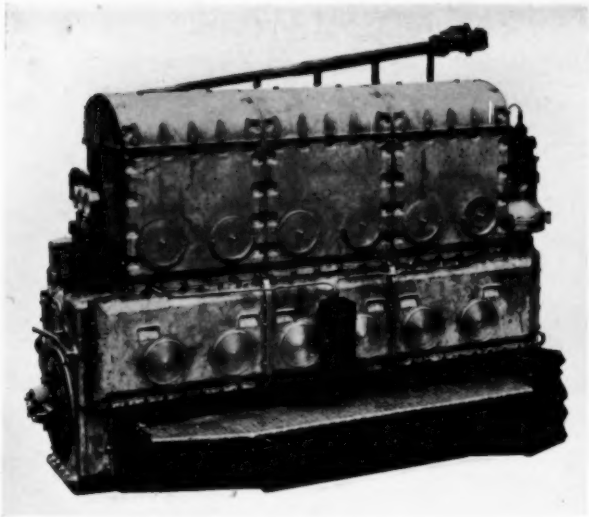

FIG. 10.

ARMSTRONG SULZER 6-CYLINDER ENGINE FOR OIL ELECTRIC RAIL-COACH.

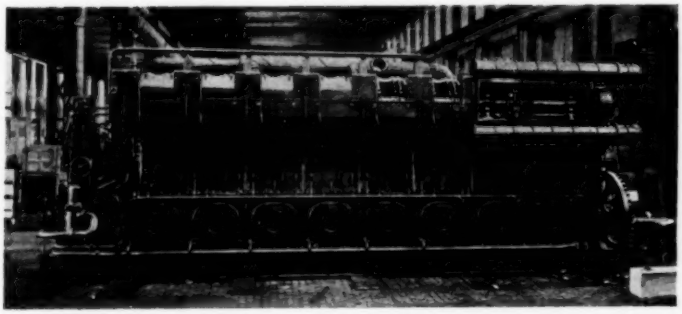

FIG. 11.

M.A.N. 6-CYLINDER DIESEL ENGINE AND AIR COMPRESSOR FOR DIESEL-COMPRESSED AIR LOCOMOTIVE. 1200 B.H.P. AT 450 R.P.M.

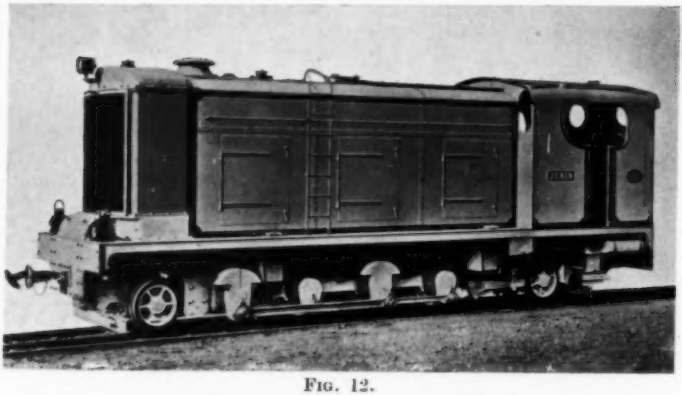

FIG. 12.

HUDSWELL CLARKE 330 B.H.P. DIESEL LOCOMOTIVE WITH MECHANICAL TRANSMISSION.

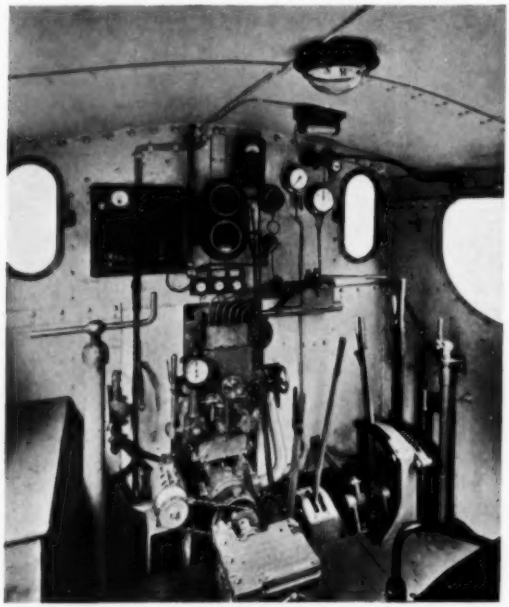

FIG. 13.

HUDSWELL CLARKE 330 B.H.P. DIESEL LOCOMOTIVE. VIEW INSIDE CAB.

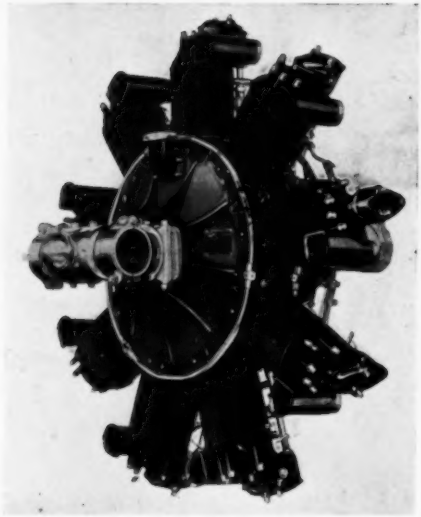

FIG. 14.

PACKHARD-DIESEL AIRCRAFT ENGINE. 9-CYLINDER. 225 B.H.P. AT 1950 R.P.M.

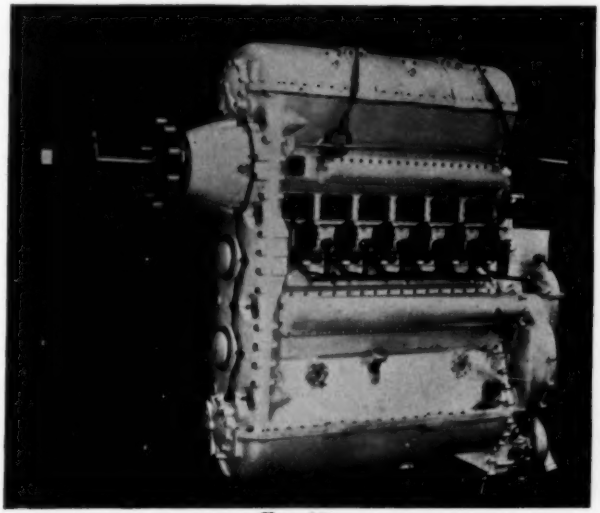

FIG. 15.

JUNKERS "JUMO 4" HEAVY OIL AERO ENGINE. 6-CYLINDER. 720 B.H.P.

The following figures are interesting as showing the extent to which it is possible to reduce weight and size. They refer to engines actually in service to-day, direct coupled to dynamos. Both engines are 4-stroke, high compression type :—

B.H.P.	R.P.M.	Cylinders.	Injection.	Length.	Height.	Weight with Flywheel.
300	175	3-18″ x 26″	Air	17′ 0″	12′ 10″	60.25 tons.
300	900	6-7½″ x 12′	Airless.	9′ 9″	5′ 10″	6.25 tons.

Marine Engines.

Four-stroke and 2-stroke cycle engines of both single and double-acting types continue to be built.

The largest marine engines completed during the period under review, namely, the twin-screw sets for the White Star Liner "Georgic," are similar to those fitted in the "Britannic," being 4-stroke cycle, double-acting, each engine 10 cylinders, 10,000 B.H.P. at 110 r.p.m., air injection, cylinders 840 mm. × 1500 mm., but the number of such type engine building is decreasing, while the number of 2-stroke cycle double-acting engines is increasing, and there is every indication of rapid development in the use of this latter type engine for horse powers of, say, 5000 and upward. This type engine has been designed and installed by M.A.N., Richardsons & Westgarth, A.E.G., Burmeister & Wain, Sulzers, and others, while many firms can build such engines under license.

Although Sulzers have always been one of the leading firms building 2-cycle, single-acting engines, it is only recently they have put a double-acting engine into service : this was in the M.S. "Tajandoen." The engine has 8 cylinders, 700mm. × 1200 mm., developing 7600 B.H.P. at 106 r.p.m. A reciprocating scavenge pump is driven from the crankshaft and air injection is used for the fuel. This engine weighed 200 tons less than the corresponding 2-stroke cycle, single-acting engine. In the middle part of the cylinders are the ports. On one side are the exhaust ports, one horizontal row for the top end and a similar row for the bottom end. At the opposite side is a central row used alternately for scavenging both top and bottom ends, with an extra row of ports above and below for charging.

A most interesting marine plant is that produced by the M.A.N. Company for the German pocket battleship "Deutschland." This is the first motor battleship, and at the same time also the largest marine installation in the world. The ship has twin screws each driven by 4 engines, coupled to the shaft through a combination of gearing and hydraulic couplings, that is, there are 8 main engines. The engines are 2-cycle, double-acting type, each developing 7100 B.H.P. at 450 r.p.m. in 9 cylinders, 420 mm. × 580 mm., and using airless injection of the fuel. Four similar engines with five cylinders are used for driving the scavenge air blowers. Thus the total horse power in the ship is about 70,000 B.H.P.

The general design of the engine is steel plate framing electrically welded with an arrangement of vertical bracing bolts, resulting in the usual bed plate casting being unnecessary. By such means the weight of the bare engine has been reduced to the remarkable figure of 17·6 lbs. per B.H.P.

The M.A.N. Company have now built or are building about 700,000 B.H.P. of 2-cycle, double-acting marine engines for merchant ships. This engine is built by Vickers-Armstrongs in this country.

Of other new engines recently completed may be mentioned the Burmeister & Wain 2-cycle, single-acting engine. This has an arrangement of scavenging ports similar to that used in their 2-cycle double-acting engines, also the Jorgensen 2-cycle double-acting engine built by Earles, but so far this latter engine has not been put into service.

The distinguishing feature of the various 2-cycle engines, both single acting and double acting, is the design of the scavenge, charging and exhaust ports, and in analysing results obtained from the various engines it would appear there is still much to be done in this direction.

A recent case of supercharged 4-cycle, single-acting engines is the twin-screw M.S. "Polyphemus" engined by Scotts. Each engine has 6 cylinders, 620 mm. × 1300 mm. with air injection, developing 2750 B.H.P. at 138 r.p.m. Supercharging is by means of a centrifugal blower driven by a gas turbine in the main engine exhaust pipe.

One of the principal oil companies now has 18 tankers fitted with supercharged 4-cycle single-acting engines of Werkspoor design.

Diesel electric drive for ships has not advanced, and only a few such installations have been delivered.

The fishing trawler is about the only class of ship in which the Diesel engine has made little headway; in fact, the only Diesel trawlers so far built have all been for continental owners and for special work at a long distance from the base. For this work they are ideal, due to the increased radius of action. There are, however, indications that Diesels will be fitted to ordinary trawlers in the near future.

For small craft the petrol and kerosine engine is being rapidly displaced by the high speed Diesel engine as made by Gardners, McLaren Benz, Gleniffer and many other firms.

Engines for Road Vehicles.

The most spectacular development has been in this section. Oil engines have for some time been used for tractors, road rollers and such work where the r.p.m. of 800 to 1000 or even lower is satisfactory, but for driving goods and passenger vehicles on the road

something better is required. The early engines suffered from being too small and too light for their duty. Mercedes Benz were the first to realise the conditions, and the engine they produced and standardised in 1928 is still in production and giving satisfaction. At the present time there are about 15 different high-speed Diesel engines being produced in this country alone for transport work, and several more in other countries. The firms, however, that probably have the most road experience in service are Mercedes Benz, Saurer, Gardner, Deutz, A.E.C.

All five engines are of different design, and particulars are as follows :—

Name.	Cyls.	B.H.P.	R.P.M.	Diam. m.m.	Stroke m.m.	Lbs./ B.H.P. Weight.	Type.
Mercedes Benz ..	6	85	1650	105	165	18	Prechamber (central).
Saurer	6	83	1600	110	150	18	Acro Expansion Chamber.
Gardner	6	102	1700	108	152	15	Direct Injection.
Deutz	6	80	1300	115	170	25	Prechamber (Eccentric).
A.E.C.	6	130	2000	115	142	11.1	Separate Combustion Chamber.

At the present time there is a considerable difference between the price of petrol and Diesel fuel, and it is this difference that has given the impetus to the application of the oil engine to road transport, but it is on a basis of fuels at equal prices that the oil engine must and can prove itself. On this score of economy the direct injection type as made by Gardner's shows up to advantage both on the test bed and more so in service. The fuel consumption curve is much flatter than that of a petrol engine, and varies little from half load to 10 per cent. overload. In service 100 to 120 gross ton miles per gallon is a good average figure for a heavy petrol vehicle. The direct injection engine (Gardner) is giving 180 to 200 and over, and those fitted either with prechamber or expansion chamber about 150 to 160. For carrying loads, say, of 5 tons and upwards for, say, journeys of 200 miles and over, the oil engine now appears to be firmly established. In addition, many of the large municipalities are much attracted by the oil engine driven bus, notably Manchester, who have a fleet of 36, mostly fitted with Crossley engines. Several other municipalities are trying out various types. A Gardner engine double-deck bus in Leeds has averaged 12·4 miles per gallon of fuel over a distance of 30,000 miles, being about one-half the consumption of the corresponding petrol engine buses over the same route. There are now approximately 500 Diesel vehicles on the road in this country.

The United Kingdom has probably more experience in this line than any other country. There is also considerable interest shown in Germany, where there is probably about the same number of vehicles on the road as here, the great majority being Mercedes Benz, also some Deutz, Büssing, Junker, M.A.N. In France, Renault have produced an oil engine, but most of the vehicles on

the road are Saurer, from Switzerland, or Junker made in the Peugot works. So far the United States have shown little interest in the subject, the Cumming engine being the only one to make a name. This engine is of the 4-cycle direct injection type, with a special system of fuel injection suitable for high speeds. The cylinders are $4\frac{7}{8}$ ins. $\times$ 6 ins., and the engine develops 125 B.H.P. at 1800 r.p.m. in 6 cylinders, the weight being 1950 lbs. This is probably the first Diesel engine to be fitted to an ordinary motor car with success. With the exception of Junker, all successful engines have so far been of the 4-cycle type. Petters have, however, developed a 2-cycle high-speed oil engine with direct injection, to give 36 B.H.P. at 1200 r.p.m. in 3 cylinders, $4\frac{1}{2}$ ins. $\times$ $5\frac{3}{8}$ ins., which has given very good results under service conditions. The maximum speed is 1600 r.p.m. There are scavenge pumps of the positive piston type to each cylinder driven by chain from the crankshaft, running at engine speed and delivering through ports in the cylinder side.

The Michel engine in Germany is also a 2-cycle engine, having 3 cylinders arranged radially with a common combustion chamber. These units of three are placed side by side and drive on to three crankshafts, which are all coupled together. An 80 B.H.P. engine has done about 25,000 miles in a 5-ton lorry with very good results.

Some engineers consider that the pressures in the compression ignition engine are too high, and are seeking to burn heavy fuel in low compression engines. These consist broadly of engines where the fuel is vaporised before it enters the cylinders, such as the Godward Vaporiser, and engines in which the liquid fuel is pumped or fed into the cylinder inside which there is some form of internal vaporiser such as the G.F.K. and the Scott. The compression pressure in all these engines is the same as in a modern petrol engine, and consequently the air cannot ignite the initial charges without some aid, which is usually magneto and sparking plug, and petrol is used for starting. Thus it is necessary to carry two fuels. A great deal of research has been done on such type engines, but so far they have all been very sensitive to variation in fuel quality, and fuel consumption is higher than in the high compression engine.

Engines for Locomotives.

A great deal of experimental work has been carried out by the leading Diesel engine builders in conjunction with the railway engineers in almost every country in the world. The engine can be either 2- or 4-cycle, air or airless injection, but experience points to it having not less than 6 cylinders and its weight being about 30–32 lbs. per B.H.P. For many reasons, such as head room, there is a limit to the B.H.P. per engine, but there is no reason

why the total power installed should not equal that required for the largest American locomotive of 6000 B.H.P. At present, the largest oil engine locomotive in the world was built by Beardmore for the Canadian National Railway, and has two engines, each 1330 B.H.P. Several oil engine locomotives are in hand at Sulzers and Frichs, Denmark, fitted with 2 – 850 B.H.P. engines. These are for the Siamese Railways and the Buenos Ayres Great Southern Railway. All the above are fitted with electric drive. A typical oil engine electric rail coach is just about to be put into service on the L.N.E.R.

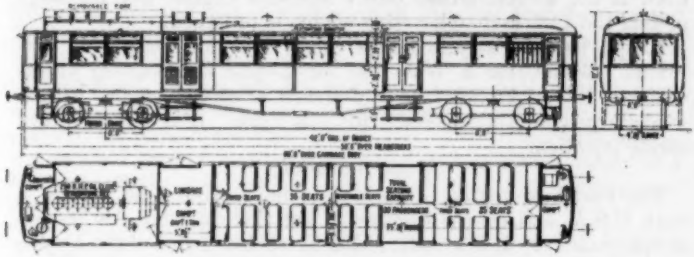

FIG. 9.

GENERAL ARRANGEMENT OF THE ARMSTRONG WHITWORTH OIL ELECTRIC RAIL-COACH.

This coach is fitted with engines of Sulzer type, built by Armstrong Whitworth, and has already undergone successful trials. The motive power is a 6-cylinder, 4-stroke cycle, high compression, pre-chamber engine, developing 250 B.H.P. It has a monobloc cylinder casting bolted to a fabricated steel crankcase. Steel liners and aluminium pistons are used, and generally the engine is light-weight type specially designed for locomotive work.

In addition to oil engine electric drive, the M.A.N. Company also build an oil engine locomotive with compressed air transmission. The engine drives an air compressor, the discharge from which is superheated by the engine exhaust. The heated air is then used in the cylinders of the locomotive in a similar manner to steam. A 1200 B.H.P. locomotive of this type has been in use on the German State Railways for some two years.

Krupp also have developed an additional type to the oil engine electric drive. In their design, mechanical gearing is used in conjunction with hydraulic clutches, and in addition the gear changing is carried out by pneumatic clutches specially designed to eliminate the " snatch " with ordinary gears. A locomotive of this type driven by a 1200 B.H.P. engine has been running comparative tests against one with electric drive on the Russian Railways.

In this country Hudswell Clarke, Leeds, built for the Compania de Salitres y Ferrocarril de Junin, Chile, a 330 B.H.P. oil engine locomotive in which the drive was through a Vulcan Sinclair coupling and gear box. The engine was supplied by the M.W.M., Mannheim, and developed 330 B.H.P. at 100 r.p.m. in 6 cylinders, 205 mm. × 270 mm., and was of the 4-cycle high compression pre-chamber type. Gear changing was facilitated by a synchronising gear lead into the cab.

The engine usually supplied by M.A.N. Company for locomotive work is the 4-cycle airless direct injection engine, but for large powers the 2-cycle double-acting engine is proposed.

Krupp use the 4-cycle airless direct injection design, as also Frichs. Burmeister & Wain use the 2-cycle single-acting airless engine. Davey Paxman have designed a special engine with a welded-up framework specially for this work. It is 4-cycle airless spring injection.

Aero Engines.

The Packhard engine is reported to have given good service in both U.S.A. and on the Continent, but there are none in service in this country. It is a static radial air-cooled engine of the 4-cycle type, direct injection, with 9 cylinders, 4–13/16ths ins. diameter and 6-in. stroke. Rated 225 B.H.P. at 1950 r.p.m., weight 2·26 lbs. per B.H.P.

The Junker engine is also in service, several engines being in use in freight machines in Germany. This is a water-cooled engine with two opposed pistons working in each cylinder and two crankshafts geared together. There are 6 cylinders of 120 mm. bore arranged vertically in line. It is a 2-cycle engine with direct injection, rated 720 B.H.P. at 1700 r.p.m. The weight of the complete engine is 800 kg.—that is, 2·34 lbs. per B.H.P., and the fuel consumption 0·371 lbs. per B.H.P. hour.

In this country Napier, Rolls-Royce and others are working on the problem, and there is little doubt that in due course they will produce engines at least equal to any other Diesel Aero engine. It is less certain, however, that the Diesel Aero engine in its present form will ever be able to put up a performance equal to that of the Rolls-Royce spirit engine used in the Schneider Trophy contest.

For airship work, weight is not quite so important. In this country the Beardmore water-cooled 4-cycle direct injection engine has been used for this purpose. Each engine had 8 cylinders, 8¼ ins. × 12 ins., and was rated at 650 B.H.P., at 1000 r.p.m., and weighed about 8 lbs. per B.H.P.

Both Mercedes Benz and Maybach are reported to be working on Airship Diesel engines for the new Zeppelin.

Our thanks are due to the various manufacturers for permission to publish information and for the use of various photographs.

Asphalts and Road Materials.

By F. Levy, A.I.C. (Member).

General.

The commercial situation with regard to bituminous material reflected very clearly general industrial conditions. Low prices, decreased demand and over-production were the main factors, and the larger companies made strenuous efforts to obtain some measure of rationalization and to supply in all cases from the nearest convenient point. There has, however, been little, if any, curtailment of production, but new sources of bitumen, both synthetic and natural, are being opened up without any corresponding increase in the demand for industrial purposes and with every possibility of a decrease of the road requirements due to drastic Government "economies" in this and other countries.

The statistical information available in Europe is scanty, in comparison with the comprehensive statistics published in the U.S.A. In *Mineral Industry*, Vol. No. 39, 1931 (published by the McGraw-Hill Publishing Co., Ltd., of Aldwych House, London, W.C. 2), Hubbard gives the American figures for export country by country, production and sales of all types of asphalt, together with the manufacture of asphalt at the U.S. refineries of the various types for paving, roofing, cutbacks, etc. It is interesting to note that the production of petroleum asphalt for paving was 1,480,316 tons, and 937,554 tons of road oil. Roofing was responsible for the consumption of 1,158,025 tons of asphalt and flux.

Nomenclature.—A certain measure of agreement on the question of nomenclature has now been reached by the International Committee, which has brought the definitions more or less into line with the accepted American specifications.[1] The advisability of a definition based on the solubility in carbon bisulphide, however, is boldly challenged by Graefe,[2] who compares the present "International" classification with those made by Mallison and by Abrahams and considers the present one of no commercial value. The point is well worthy of further thought, for finally it is the user who must be induced to employ the terminology devised for him by the technician; therefore, until the sales side of the industry is brought into co-operation and until an educative campaign is devised, progress is bound to be slow.

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[1] *Petr. Times*, 1931, **25**, 414.
[2] *Asphalt und Teer*, 1931, **31**, 877–881.

Chemical.—Little has been published during the year with regard to the constitution of bitumen, although important investigations are in the course of completion. Nevertheless, Stadnikov and Wahner's notes[3] on the nature of coal bitumen are a useful summary of the subject, and also the brochure issued by the South Metropolitan Gas Company, giving the results of Evans and Pickard's work.[4] In this connection reference should be made to the series of articles in *Asphalt and Teer*, by Klinkmann, on the properties of tar-bitumen mixtures. This author shows that with additions up to 15 per cent. to a tar, the asphalt acts as a stabiliser, 15-35 per cent. as a coagulant, and in mixtures of over 35 per cent. the bitumen serves to peptise the tar dispersion.[5]

An account of the ultra filtration of asphalt in the endeavour to separate paraffins from asphalt (the latter being recovered quantitatively) is also recorded as demonstrating the colloidal structure.[6] Nellensteyn, continuing his now well-known work on "The Surface Tension of Bitumen at Various Temperatures," prefers a method of pressing a bubble of inert gas (N.) through a capillary tube dipped in the molten material.[7] Determinations on various types of bitumen carried out at different temperatures show that surface tension increases rapidly with diminishing temperature, but for each substance there is a significant temperature called the "deflection point" above which the material behaves (as shown by the curves) very much like the ordinary heavy lubricating oil, whilst below that point the cohesion is very much decreased. The deflection point of Spramex is given as 117° C, Trinidad Epuré, 132° C. and Pitch as 80° C.[8]

Meanwhile, the historical aspect of bitumen is touched upon in an interesting note by Graefe on the "Kuffa," or bitumen-built boats of Iraq,[9] and also in a short paper by Hackford and others on "An Asphalt Ring from Ur of the Chaldees."[10]

Rock Asphalt and Natural Asphalt.

Two forms of natural asphalt which have become staple articles of commerce are of general interest. They are Iraq Asphalt and Boeton Asphalt.

The former takes the form of boulders containing an unusually high percentage of bituminous matter (*i.e.*, 80). The specific

[3] *Brenn.-Chem.*, 1931, **12**, 23–25.
[4] *Surveyor*, 1931, **79**, 584.
[5] *Asphalt und Teer*, 1931, **31**, 1158.
[6] *Bull. Soc. Chim. România*, 1930, **12** (90), 4.
[7] *Kolloid-Chemische Beihefte*, 1930, No. 34, p. 434.
[8] *Roads and Road Constr.*, 1931, **9**, 127.
[9] *Asphalt und Strassenbau*, 1931, **25** (12), 3–5.
[10] *J.I.P.T.*, 1931, **17**, 738–740.

gravity of the asphalt is 1·28 and its melting point 80·5° C, and the inorganic residue consists of 85 per cent. $CaCO_3$ and 15 per cent. SiO_2.

Boeton Asphalt, however, appears to be impregnated globigerina found in connection with the limestone and lime marls of which the island consists and which it is thought were deposited at a depth of 2000-6000 metres. The bitumen content is 37-39 per cent., has a specific gravity of 1·09-1.11, a melting point (R. and B.) of 61·69°C., and contains 6-7 per cent. of Sulphur.[11]

Much useful information on the natural asphalts has been published during the year, including a booklet by Vose and Swell, entitled "Rock Asphalt and its Uses," a description of the more modern uses of Trinidad Asphalt for acid-proof flooring for chemical factories, etc.,[12] and a short note on Manjak.[13]

Of still greater importance, however, was a paper delivered to the Chemical Engineering Group of the Society of Chemical Industry by Donald M. Wilson. Dealing mainly with Val de Travers, the author describes the four standard forms of paving; Compressed Asphalt, Asphalt Slabs, Mastic Asphalt and Steam Rolled Asphalt. Of very special interest, however, were the methods of testing, to which reference will be made later.

Levi and Collins report on the design and working of a plant for fractionating the distillate obtained from Ragusa and Abruzzo Asphalts[14]; similarly La Porta[15] records that the former contains 40-65 per cent. of material of high calorific value, the bitumen consisting of 84·9 per cent C, 11·7 per cent. H and 3·4 per cent S. Distillation results are given and it is shown that by cracking, 50 per cent. of light distillate may be obtained. An interesting proposal for the hydrogenation of the bitumen contained in Alberta Sands is made by Boomer and Saddington. The bitumen (Sp. Gr. 0·9984, S 4·16 per cent.) is first separated and then hydrogenated at about 380° C. with or without catalysts (Am. Mol. & Al_2Cl_6); 3 per cent. of H. is taken up and 80 per cent. of light crude oil results.[16]

Petroleum Bitumen.

Refining.—The chief feature recorded with regard to refining has been the bringing into line of plant for the preparation of asphalt with the general tendencies of modern distillation practice.

[11] *Asphalt und Teer*, 1931, **31**, 831–833.
[12] *Chemical Trades J.*, 1931, **88**, 316.
[13] *Oil and Colour Trades J.*, 1931, **80**, 1177.
[14] *Chem. Abstr.*, 1931, **25**, 2391.
[15] *Mineraria*, 1931, **5**, 65–77.
[16] *Brit. Chem. Abstr. B.*, 1931, 467.

The most important change is the adoption of the vacuum flash coil whereby closer fractionation of asphaltic crudes may be obtained.[17]

Generally speaking, asphaltic or mixed base crudes are first treated by a single flash system so as to obtain the lighter fractions, and the reduced crude is then flashed into a tower under vacuum, whereby heavy gas oil, cylinder stock and wax distillate are taken off. Bancroft[18] describes the preparation of asphalt from Smackover crude, water and a small amount of gasoline being first removed under partial vacuum in a dehydrator. By heat exchange the temperature of the crude is raised to 360°C. and then pumped to a second evaporator and a bubble tower. The residues pass through a further series of coils and at a temperature of 405°C. go direct to the vacuum tower, where they are flashed under 27½ mm. absolute pressure. From the top of the tower a lub. oil distillate is removed. Standard grades of asphalt are produced for all various purposes and a useful flow sheet accompanies the article.

The whole system of fractional distillation is the subject of a very interesting article by Edmonds.[19] In this connection a Royal Dutch Patent[20] deals with the recycling of the heated residues whereby they serve as heat carriers to the incoming material, whilst Crothers[21] holds a patent for reclaiming asphalt from cracking plant residuals by mixing with fuel oil—the free carbon is thus settled out—and after separating by centrifuge the asphalt is reduced.

The production of what might be called "Synthetic Petroleum Asphalts" from crudes generally considered non-asphaltic, such as Pennsylvanian and Mid-Continental, is interesting. Egloff and Morrell[22] prepared such asphalts, which are characterised by a high specific gravity and a high loss in penetration on heating. In an important paper given before the Institution of Chemical Engineers, Taylor describes the plant necessary for the production of some four tons daily from cracked fuel oil of R.II 345 at 100°F. received hot from a cracking plant. Temperatures and yields are given in full for asphalt of a hard variety sufficiently brittle to be run into a pit and then broken up. In contrast to Egloff and Morrell, Taylor uses large quantities of air in blowing and hence his products take on the character of normal blown bitumen.

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[17] *Refiner*, 1931, **10** (8), 80.
[18] *Oil and Gas J.*, 22.1.31, **29** (36), 30.
[19] *J.I.P.T.*, 1931, **17**, 425–450.
[20] E.P. 361,173.
[21] U.S.P. 1,788,792; *J.I.P.T.*, 1931, **17**, 275A.
[22] *Ind. Eng. Chem.*, 1931, **23**, 679.

With these methods available and fuel oil at a low price it is not surprising to find users of bitumen erecting plant to supply their own needs rather than purchasing from the oil companies. Quite an extensive plant of this nature was installed during the year at Dundee.[22]

Another method of obtaining asphalt is to produce it from refinery residues. Allen[24] treats Edeleanu Extract, etc., preferably after removal of constituents boiling below 250°C., by blowing hot air whilst heating in an autoclave. He claims great ductility for his final products, but from the figures given no great superiority over the ordinary steam-run or refined products is discernible at the lower temperature ranges. There is also a German patent[25] for treating distillation residues at about 250°C. with a mixture of S and H_2SO_4 so as to decompose the acid, and a further one by Bolgar[26] for treating oil with H_2SO_4 at 250-350°C., and then blowing until all the SO_2 has been expelled.

Blowing.—An interesting article by K. W. Nielsen[27] is intended to refute the charge that blowing impairs the quality of the bitumen, and he gives details of bitumen made from various crudes showing the low ductility obtained with products made from Mid-Continental oil and the correspondingly satisfactory asphalts got from Panuco crude, from which he concludes that it is necessary to use an asphaltic or mixed base crude as the starting point, and that bitumen produced by distillation at high temperature is not likely to be satisfactory. He gives an interesting table and set of figures in support of his contentions.

The use of chlorides, sulphates and carbonates of iron, copper, and antimony is proposed by Abson[28] for reducing the temperature of blowing.

Treatment.—Variation of the properties of bitumen in order to make them more desirable for special purposes has received much attention during the year. Lichtenstern heats asphalt with China wood oil and aluminium chloride, etc., and obtains (without the use of sulphur) an extremely elastic and infusible product.[29] The Bataafsche Petroleum Maatschappij propose to make bitumen less sticky by addition of resinates, sulphonates and naphthenes,[30] whilst Anderson and Child purify bitumen by dissolving and

[22] *Chem. Trade J.*, 1931, **89**, 12.
[24] E.P. 362,580.
[25] G.P. 517,166.
[26] G.P. 523,419.
[27] *Asphalt und Teer*, 1931, **31**, 881–2.
[28] U.S.P. 1,782,186; *J.I.P.T.*, 1931, **17**, 50A.
[29] G.P. Apl. L, 73,967.
[30] E.P. 355,430; *J.I.P.T.*, 1931, **17**, 508A.

adding a colloidal substance such as silicic acid and subsequently decanting and redistilling.[31] The use of bauxite and bauxite residues has also been proposed.[32]

Application.

Road-Building.—Echoes and reactions of the Sixth International Road Congress were still heard during the year, and an interesting summary is given by Spielmann,[33] restating the Resolution passed by the Congress with regard to the suitability of tar and bitumen for road work and laying down the governing conditions of such application. The problems for research and the need for an international classification are also set forward in the Resolution. Hoepfner also reports in greater detail.[34]

The New International Association for Testing Materials published a paper on the significance and measurement of surface forces, whilst papers were presented to the first conference, by Suida and Janisch of Vienna, dealing with nomenclature and methods of analysis, including curves of penetration and ductility to illustrate thermic stability; Hubbard and Reeve on methods of analysis, and Weiss and Woog, the latter advocating the use of absolute units for the measurement of viscosity.[35]

The Road Show in November, though not perhaps so informative with regard to new materials, was of special interest as exhibiting the great progress which has been made by the British manufacturers of roadmaking machinery with plant adapted for all types of work under all conditions of soil and climate; the needs of the newer and more undeveloped countries were specially well catered for. At the corresponding function in Paris—La Semaine de la Route—some interesting papers were read, including that of Conche on "Le progrés récent dans le confection de liants hydrocarbons."

The general value of asphalt and the important part which it has played and is playing in the improvement of the motor road were well stated by Agnew in an address to the Oil Industries Club.[36]

Two features of importance were prominent during the year. The first is the treatment of earth roads with asphaltic oils and similar substances whereby they are made to bear ordinary motor traffic at all seasons of the year. In North and South America, India, Egypt, Syria, South Africa and Australia there are tens of thousands of miles of tracks which would never be paved had it

[31] E.P. 339,470; *J.I.P.T.*, 1931, **17**, 93A.
[32] G.P. Appl. A. 58,596 and E.P. 356,797.
[33] *J.I.P.T.*, 1931, **17**, 183–184.
[34] *Asphalt und Teer*, 1931, **31**, 295–303.
[35] *Rev. Gen. Routes*, 1931, **6**, 321.
[36] *Petr. Times*, 1931, **25**, 859–860.

meant bringing road metal or aggregate to the site, but by treatment with suitable machinery, *i.e.*, furrowing the loose earth, treating it with oil or emulsion, regrading and shaping, it is possible to form a sufficiently hard crust on these roads to take the traffic.[37] They cease to be dust storms in summer and mud puddles in winter, and places situated at huge distances apart and hitherto almost inaccessible will now be placed in communication. In America specialised machinery for this purpose has been developed. In England there is not likely to be a great demand for earth roads; stone is plentiful and the earth is generally much too sodden and often too clayey. Nevertheless, some work has been done on similar lines in order to provide landing grounds at aerodromes. For this purpose emulsions have been chiefly employed, and the work at Croydon Aerodrome presents a remarkable example of what is possible in this direction.

The second of the features referred to above has a more local interest, viz., the prevention of skidding. This problem is still greatly exercising everybody's mind, as is shown by Col. Bressey's note on the Experimental Surfaces put down by the Ministry of Transport at Colnbrook, and also his very wise insistence of the personal factor in the matter.[38]

The Asphalt Roads Association has taken up the question in a very practical way and British Standard Specifications have now been drafted for giving asphalt roads a roughened surface by spreading over the asphalt, whilst it is still warm, $\frac{1}{2}''$ to $\frac{3}{4}''$ chippings which have been previously coated with 2 to 3 per cent. of a bitumen of medium penetration. They are applied at the rate of one ton per 120 sq. yds. and well rolled. Similarly, on existing smooth surfaced roads, the application of precoated large size chippings has gone far to solve the problem. For all classes of surface dressing the large chipping is almost a *sine qua non*.

In connection with roads more attention is being devoted to the types of stone employed from the scientific and geological standpoint, as evidenced in the lecture delivered to the Faculty of Engineering at Liverpool University by Lionel V. Barton, Dr. Knight's paper on British Whinstones,[39] and Morton on "Properties, Selection and Specification of Sandstones."[40] How important the function of the stone can be is also shown by a communication by Neumann and Wilhelmi of the University of Stuttgart, dealing with the adsorption of bituminous binders by road stones and detailing a colorimetric method of determination.

[37] *Roads and Road Constr.* (T. W. Allen), 1931, **9**, 12–14.
[38] *Surveyor*, 1931, **79**, 566.
[39] *Surveyor*, 1931, **79**, 579.
[40] *Roads and Road Constr.*, 1931, **9**, 189–191.

This has been translated by Spielmann, who considers the subject of vital importance.[41] Ebberts has also published a paper full of thought on the emulsifying action of asphalt fillers.[42]

Spielmann comments on the present situation as regards the range of sieves adopted by the B.S.I., and in addition he gives a useful table of comparison,[43] but the subject is even more complicated in making comparisons with the Continent, where the D.I.N. Specifications are in use.

Hoepfner[44] sets out to investigate : (*a*), an accurate method for determination of the solidifying point ; (*b*), the co-relation of viscosity and softening point ; and (*c*), the co-relation of viscosities for both bitumens and mixtures. He considers the solidifying point of importance, "since bituminous substances when solidified become brittle and lose binding power. . . ." He has devised a very elaborate method of measuring penetration, and from the solidification point he is able to correlate viscosities under a relationship 1·37E=350 degrees H.M., *i.e.*, 200 ml. of any bituminous substance of 350 degrees H.M. requires 1·37 times as much time as 200 ml. water to flow through an Engler viscometer. From tables prepared, the temperature to which any given substance must be heated to obtain the viscosity of water can be interpolated.

In connection with viscosity measurements an ingenious falling sphere method with electrical contacts is proposed by Broome and Thomas.[45]

Dr. Wichert[46] contributes a very timely article drawing attention to the investigation of the weathering properties of asphalts, and these ideas also underlie an informative article on bituminous construction by the same author[47] who also deals with the specific tests and their lack of significance. The subject of accelerated weathering tests is also treated by Strieter,[48] who describes the three carbon arc lamps employed. It is found possible to classify asphalts according to behaviour, and such classification is assisted by analysis, since it is established that oil and resin content are found to decrease on weathering and asphaltenes to increase.

Attwooll and Broome write on the reciprocal value of bitumen and tar in road construction,[49] and they stress the advantages to

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[41] *Roads and Road Constr.*, 1931, **9**, 402.
[42] *Roads and Road Constr.*, 1931, **9**, 124.
[43] *Roads and Road Constr.*, 1931, **9**, 233–234.
[44] *Roads and Road Constr.*, 1931, **9**, 17–19, 61–63, 84–86.
[45] *Chem. and Ind.*, 1931, **9**, 422.
[46] *Asphalt und Teer*, 1931, **31**, 1205.
[47] *Asphalt und Teer*, 1931, **31**, 643–647.
[48] *J.I.P.T.*, 1931, **17**, 274A.
[49] *Roads and Road Constr.*, 1931, **9**, 303.

be gained by mixing tar and bitumen, but prefer to add Trinidad asphalt on account of the colloidal matter contained, whilst Nellensteyn[50] gives methods for a more scientific control of such mixtures.

Special methods of treating or applying asphalt are now very numerous and amongst others should be noted those of Hack, who uses bitumen in a foam-like form,[51] and also the Amber Size and Chemical Company's proposal[52] to add oxy aromatic, nitro and amine compounds (a somewhat wide range) to increase the covering power.

The use of *Rubber* as a surfacing material has not extended as much as might have been expected in view of the low prices now prevailing. Numerous Patents have, however, been granted for various improved methods of application.[53] In the rubber producing countries, however, (Dutch East Indies, Federated Malay States, Ceylon, etc.) extended trials are being made of previously patented methods of using combined bituminous rubber emulsions, and to date promising results have been obtained.

Tar.—It is beyond the scope of this summary to deal at any length with tar, but the more important features should not escape mention. For the last year or two there has been a genuine attempt to improve quality, technique and service, and also towards standardization on really useful lines.[54] This is not only true of this country but in Germany[55] also, where the consumption has risen from 3,000 tons in 1924 to 40,000 tons in 1930 (asphalt being 100,000 and 250,000 respectively), the movement has been felt.[56] At the same time Germany still only employs 7 per cent. of her tar for roadwork, as against 40 per cent. in England (doing a large export trade), 62 per cent. in France and 78 per cent. in the U.S.A.

The so-called "Cold Tars" which were so popular in Germany at the end of 1930 and the beginning of 1931 have not so far invaded this country, but the numerous asphalt surfacing compounds (often a mixture of bitumen and tar oils) which have appeared on the market here, may be said to be in counterpart.

A good deal of excellent technical work has recently been published on tar and similar compounds. Evans and Pickard's work has already been referred to; there is also an excellent article by Pickard on considerations affecting the use of tar for

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[50] *Koll.-Chem. Beih.*, 1930, **31** (9), 12.
[51] G.P. 536,712.
[52] E.P. 355,937 and G.P. 556,003.
[53] E.P. 357,603, 357,699 and 358,142.
[54] British Standard Specifications, No. 76, Part 2.
[55] *Surveyor*, 1931, **79**, 314.
[56] *Chem. and Ind.*, 1931, **9**, 530.

surfacing operations.[57] Although primarily dealing with tar, the extension to other surfacing compounds is worth considering, even though in some cases the conditions do not compare with those actually obtaining on the road.

Emulsions.

Patents for emulsification in Great Britain and other countries still continue to be applied for, although the principles governing the selection of suitable emulsifiers are now well known.[58] A useful summary of the present state of the art is given by Saladini.[59] The application of emulsion to the construction of earth roads has already been dealt with, and the use of emulsion (as well as hot bitumen) for the preservation of railway tracks—below the ballasting—is becoming a matter of much importance in several countries, particularly Germany. A special form of application, combined with the use of "Trass" is claimed by Halbach,[60] whilst several patents are intended to protect special additions to emulsions or pretreatment for mixing purposes or to obtain preliminary wetting.[61] A somewhat novel addition suggested is that of sodium aluminate and similar compounds which react with CO_2 and thus cause ready coagulation when the emulsion is applied to the road.[62] A new I.G. Farbenindustrie application, covering the use of Humic Acids, extends to the preparation of emulsions at low temperatures (*i.e.*, 50° C.), and is said to give rise to very stable emulsions[63]; conversely Jacobi proposes to spread the emulsifier solutions on the road, which is then sprayed with hot bitumen.[64]

Although the use of tar emulsions is extending, they cannot yet be said to rival in popularity the better-known bitumen compounds. China[65] has a somewhat complicated patent on their preparation and there is also a German invention for treating tars with HNO_3 to produce material suitable for emulsification.[66] The question of testing and specifications for bituminous emulsions has been taken up with much energy in England, and the B.S.I. are on the point of publishing their standards.[67] The situation has been somewhat complicated by the A.S.T.M. proposed tests, especially an attempt to establish a somewhat futile calcium chloride test.[68]

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[57] *Roads and Road Constr.*, 1931, **9**, 412–415.
[58] Travers, "Mechano-Chemistry of the Colloid Mill," p. 115.
[59] *J.I.P.T.*, 1931, **17**, 217A.
[60] G.P. Appl. H. 115,468.
[61] D.P. 47,399.
[62] E.P. 350,040; *J.I.P.T.*, 1931, **17**, 434A.
[63] G.P. Appl. 32,160.
[64] G.P. Appl. I. 38,693.
[65] E.P. 351,242.
[66] G.P. 578,394.
[67] British Standard Specifications Nos. 433 and 434.
[68] *Roads and Road Constr.*, 1931, **9**, 261.

Roofing and Paints, Etc.

The new D.I.N. specifications for roofing and impregnating material have been published during the year,[69] and the revised A.S.T.M. standards have also appeared.[70] A discussion of these, and a description of the preparation of shingles is given by Weiss.[71] A note on the cause of "seediness" in asphaltum appears in the new periodical "Paint,"[72] and it is suggested that it may be due to the insolubility of the asphalt, lack of stability of the resin solution, or settling out of the driers, etc. The author concludes that only asphalt of a readily soluble quality should be used, and that the very hard high melting point type is often liable to be insoluble in the heavy petroleum solvent used as a thinner. In this connection, a claim of Novak[73] to increase the solubility of Gilsonite by heating above the melting point and holding it for some time at that temperature, is worthy of note. The precautions and limitations of asphalt as a basis for paint are set forth by Richter,[74] who discusses the occasions on which it can be most advantageously employed.

The use of bituminous emulsions for industrial purposes has not made the marked advance witnessed on the other side of the Atlantic. A somewhat novel proposal is their use (with or without graphite) as lubricating mediums for hot moving surfaces.[75]

Specifications and Testing.

The seven new simplified specifications of the Asphalt Institute of the U.S.A. for liquid asphalt road material are discussed by Hubbard.[76] Asphalt is divided according to its use: (1) dust layer; (2) primer; (3) mix-in-place, requiring warming; (4) mix-in-place with dense wearing courses; (5) surface treatment and retread; (6) cold patch; (7) roller compacted mix-in-place. The tests given are Engler viscosity, distillation and tests on the residue.

An exhaustive series of specifications for highway material has also been issued by the American Association of State Highway Officials. Most of the methods for testing asphalts follow the A.S.T.M. fairly closely. In connection with testing, Spielmann writes an interesting article on his tour of the U.S.A., describing the various State Road Laboratories and some of those at the various Universities.[77]

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[69] *Asphalt und Teer*, 1931, **31**, 598.
[70] *Oil and Colour Trades J.*, 1931, **80**, 433.
[71] *Ind. Eng. Chem.*, 1931, **23**, 168–170.
[72] *Paint*, 1931, **1**, 69.
[73] U.S.P. 1,803,637.
[74] *Farbe und Lack Centralblatt*, 1931, **36**, 340–341.
[75] G.P. 532,802.
[76] *Surveyor*, 1931, **79**, 601.
[77] *Roads and Road Constr.*, 1931, **9**, 9–10.

Of general interest on the question of the separation of asphalt by means of solvents is an article by Poll.[78] He discusses the work previously done on the subject, and proposes a method using petroleum ether—boiling up to 50° C.—in the cold. After twenty-four hours, the so-called asphaltenes are filtered off and the solution treated with bleaching earth to remove the resins, which are subsequently recovered by means of chloroform. The precipitated asphaltenes are dissolved in chloroform and the previously used earth added to complete extraction of the "resins." Finally, extraction with a 50-50 mixture of pyridene and carbon bisulphide gives the hard asphalt; a much sharper separation is claimed by this method. J. Givaudon[79] also discusses the estimation of "Asphaltenes" using the different varieties of "petroleum ether" available.

The old problem of the separation of tar and bitumen is re-attacked by Mallison,[80] since it has particular interest for Germany. He proposes sulphonation followed by distillation, but finds that the residue is not homogeneous, and suggests working at lower temperatures. F. Macht[81] uses a quartz lamp for the same purpose, spreading the material in thin layers on glass plates; asphalts give a greenish yellow colour and tar a dark reddish brown. Benzine solutions of the materials enhance the colour differences, tar giving a distinct yellow (said to be due mainly to anthracene) and admixtures of 5 per cent. are said to be detected.

The difficulties with regard to the estimation of paraffin in asphalt have not yet been solved, and the whole ground is gone over very carefully by Wilhelmi,[82] who stressed both the uncertainty as to the presence and effect of the so-called paraffins and the various unsatisfactory methods proposed for the determination of these same. Following on Thomas and Littlejohn's work of last year,[83] Piotrowski and Burstin,[84] after discussing available alternatives, decide in favour of the Holde method. Suida and Janisch,[85] however, show how prolonged time taken in distillation increased the amount of cracking and so may invalidate the results obtained.

The inadequacy of the present standardised tests on bitumen is a subject that is yearly receiving more and more attention, and new tests are rapidly being devised to meet the needs of practical men. Wilson[86] describes a useful method for the extraction of bitumen

[78] *Erdol und Teer*, 1931, **7**, 350–352 and 366–371.
[79] *Rev. Petr.*, 1931, No. 408, 105.
[80] *Asphalt und Teer*, 1931, **31**, 598.
[81] *Erdol und Teer*, 1931, **7**, 225–227.
[82] *Asphalt und Teer*, 1931, **31**, 303–307.
[83] *J.I.P.T.*, 1930, **16**, 814–824.
[84] *Petr. Z.*, 1931, **27**, Asphalt III., 3.
[85] *Asphalt und Teer*, 1931, **31**, 503.
[86] *Chem. Ind.*, 1931, **50**, 599.

from aggregate, using a specially folded filter paper and a submerged addition of the solvent. The estimation of bitumen under these circumstances is also reviewed by Pages and Houlnick,[87] who describe various methods (Metzger's cold carbon bisulphide, Suida's Continuous chloroform, and the Zentral Stelle's process). They also deal with the recovery of bitumen from emulsions by the use of hydrochloric acid, acetone and other methods. Wilson in his lecture on "The Manufacture and Testing of Asphalt Paving Materials," already referred to, describes his method in full, and states that there is very little change in the physical properties of the bitumen after recovery. Another useful test also described therein is the "Pat Stain," whereby the number of packed filter papers stained in a press gives a measure of the excess of the bitumen in a mixture and also an indication of the amount of bitumen which is likely to be "held" by the aggregate. Further mechanical tests, such as hardness, deformation and tensile strength, are described in detail in this paper.

[87] *Rev. Gen. Routes*, 1931, **6**, 163.

Special Products.

By E. B. Evans, M.Sc., A.I.C. (Assoc. Member).

A large amount of work has been carried out during the years 1930-1931, on the miscellaneous products derived from petroleum and on their utilization in industry. A noteworthy feature of this period is the continued rapid growth of the synthetic side of petroleum chemistry, a large number of hydrocarbons, acids, alcohols, chlorinated compounds, etc., now being available for use in such diverse ways as solvents, insecticides, refrigerants and materials for soap-making. A general survey of the uses of these products is given by Conine,[1] who mentions a very large number of miscellaneous purposes for which petroleum derivatives are employed.

Reference will be made to most of the important developments in the sections on the various products, which follow.

The Acids and Bases of Petroleum.

Several investigators have recently studied the minor constituents of petroleum. In two papers[2] Holzmann and von Pilat showed that arachidic acid ($C_{20}H_{40}O_2$) occurred in the higher fatty acids of Boryslaw crude oil. They found that the phenol content of crude naphthenic acids varied from about 30 per cent. for Boryslaw kerosine to about 3 per cent. in the case of Bitkow distillate. Phenol itself was not isolated but three cresols, three xylols, β-naphthol and some trimethyl-phenols were separated. Von Braun and his coworkers, in a very long investigation,[3] have attempted to characterise the acids in petroleums from various sources. They show that the compounds belong to the aliphatic series up to C_{6-7}, and are monocyclic from C_6 to C_{12} and dicyclic from C_{12} to C_{23}. No evidence of higher complexity could be obtained. They suggest that the lower members found are the products of pyrogenic decomposition. Other substances such as ketones and ureides were also isolated.

Poth, Schulze, King, Bailey, etc.,[4] extracted nitrogen compounds from Californian petroleum, isolating 2-3-8 trimethyl quinoline. They suggest that in the Edeleanu residues from refining Californian petroleum is a vast undeveloped source of valuable nitrogen compounds. The purification of sulphonic and naphthenic acids is described in one or two patents.[5]

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[1] *Oil and Gas J.*, 11.6.31, **30** (4), 18.
[2] *Brenn.-Chem.*, 1930, **11**, 409; 1931, **12**, 41.
[3] *Annalen*, 1931, **490**, 100.
[4] *J.A.C.S.*, 1930, **52**, 1239.
[5] *e.g.* E.P. 300,264.

Antifreeze Compounds.

Olsen, Brunjes and Olsen[6] have examined the freezing-points and flow-points of "prestone" (commercial ethylene glycol), methanol, denatured alcohol and glycerol solutions. In some cases the flow-point is appreciably lower than the freezing-point and it is suggested that the flow-point determines the lowest temperature at which the solution is effective as an antifreeze.

The dangers of methanol poisoning arising from the use of this substance in motor-car radiators have been investigated at the U.S. Bureau of Mines[7] and by Yant, Schrenk and Sayers.[8] Although the investigations are not yet completed, it is concluded that the risks are small under reasonable conditions. It is recommended that the methanol should be coloured red and labelled as poisonous.

Carbon and Lamp Blacks.

Several papers have appeared dealing with the method of preparation of these substances. Plummer and Keller[9] discuss the factors controlling the production of carbon black from propane; channel heights and flame conditions (size and shape of flame and temperature of the gases) are perhaps the more important of these. Extensive tests indicate that the carbon black obtained from higher hydrocarbons has slightly more value in rubber treatment. Wiegand[10] discusses similar problems. The influence of the "combustion quotient" (Surface area/volume of flame) is emphasised, and it is shown that optimum gas pressures and heights of cooling surfaces exist for maximum yields. By working at 100 lbs./sq. in. pressure, yields of high-grade carbon black can be trebled, as has been shown by A. W. Francis,[11] using small scale apparatus.

A process has been patented for the production of carbon black by passing the gaseous hydrocarbon countercurrent to a stream of catalyst (*e.g.*, iron, nickel, cobalt or zinc oxides) at about 380° C.[12]

Plummer[13] investigated a method for the estimation of moisture in carbon blacks, by passing dry nitrogen through a mixture of the black with mineral oil and xylene and absorbing the moisture in calcium chloride. He showed this method to be inaccurate owing to interaction of oxygen absorbed in the carbon black and the mineral oil.

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[6] *Ind. Eng. Chem.*, 1930, **22**, 1315.
[7] *Chem. Trade J.*, 1930, **87**, 631.
[8] *Ind. Eng. Chem.*, 1931, **23**, 551.
[9] *Ind. Eng. Chem.*, 1930, **22**, 1209.
[10] *Ind. Eng. Chem.*, 1931, **23**, 178.
[11] *Ind. Eng. Chem.*, 1931, **23**, 612.
[12] J. Y. Johnson, E.P. 358,178.
[13] *Ind. Eng. Chem.*, Anal. Ed., 1930, **2**, 57.

The importance of the oxygen content of carbon blacks and its influence on rubber vulcanization is discussed by Johnson,[14] and the improvement of the electrical properties of insulating oils by treatment with carbon black is dealt with by Wiegand, Boggs and Kitchin.[15]

Helium.

An anonymous article[16] gives an account of a method developed at Berlin University for determining the helium content of natural gas, by treatment successively with white-hot calcium and cooled active carbon. Another paper,[17] also anonymous, deals with the suggestions of Rosendahl for the export of helium from the U.S.A. for use in airships. The U.S.A. government plant for the extraction of helium at Amarillo, Texas, is described by Seibel.[18] A purity of 98 per cent. is obtained by the process used.

Insecticides.

The quantity of petroleum oil now used for spraying purposes is quite considerable; de Ong[19] states that, in 1929, about five million gallons were used on the Pacific coast. In the same paper he discusses the properties of oils suitable for this purpose. Oils may be used either for their own toxic properties or as carriers for materials such as nicotine or pyrethrum extract. The specifications for these oils are now practically standardised and de Ong discusses the qualities which are desirable.

The examination of insecticides is described by Martin,[20] who confirms the conclusions of Gray and de Ong that the constituents of petroleum oils which are injurious to plants are removed by sulphuric acid.

Various mixtures have been patented for use as insecticides, *e.g.*, a mixture of petroleum white oils, plant extract (derris or cubé) and an emulsifying agent such as alkali sulphonate.[21] Ethylene oxide and ethylene dichloride are also attracting attention as fumigants, both of these substances being comparatively harmless to man.[22]

Fumigation is tending to displace refrigeration in the treatment of fruit and grain, being both cheaper and more effective. Ethylene oxide is, however, inflammable, and Jones and Kennedy[23]

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[14] *Ind. Eng. Chem.*, 1929, **21**, 1288.
[15] *Ind. Eng. Chem.*, 1931, **23**, 273.
[16] *Petr. Times*, 1930, **23**, 196.
[17] *Oil and Gas J.*, 18.12.30, **29** (31), 105.
[18] *Chem. and Met. Eng.*, 1930, **37**, 550.
[19] *Ind. Eng. Chem.*, 1930, **22**, 836.
[20] *J.S.C.I.*, 1931, **50**, 91T.
[21] Stand. Oil Dev. Co., E.P. 350,897.
[22] Russ, *Ind. Eng. Chem.*, 1930, **22**, 844.
[23] *Ind. Eng. Chem.*, 1930, **22**, 146.

suggest the addition of carbon dioxide to render the mixture with air non-inflammable. The carbon dioxide also stimulates the respiration of the insects, thus speeding up the action of the fumigant.

Paraffin Wax.

Continued attention has been given during the past two years to the problem of the structure of paraffin wax, in view of its importance to the preparation of good quality waxes. Ferris, Cowles and Henderson[24] found three types of structure present in wax: plates, needles and an ill-defined crystalline form—the plate having the highest melting-point for a given b. pt., and the needle type the lowest. The crystalline form is an inherent property of the compounds involved, and is independent of the solvent. Sachanen, Zherdeva and Vasilyev[25] suggest that two series of compounds are present—paraffin and ceresine; the latter series has, for equal melting-points, higher molecular weights, boiling-points, and a greater tendency to decompose on heating. Ceresines form stable mixtures with oil, and hence cannot be removed from such mixtures by sweating. Bestushew[26] favours these views. He finds that paraffin is distinguished by a distinct "banded" structure. Very rapid cooling tends to give paraffin a ceresine-like structure, leading to difficulties in filtration. Good rectification will prevent the ceresine coming over in the light machine-oil fraction. Katz[27] has carried out an extensive investigation on the crystallisation of wax. He concludes that the paraffin crystal is a six-sided plate. The needle form he considers to be only a series of plates formed in layers, this variety not being a homogeneous structure. Another study on the subject is that of Padgett,[28] who states that the crystal form is orthorhombic and divides the structures into plates, needles and a fibrous, feathery form; the plates are the most stable. Padgett concludes that high viscosity of the medium favours smaller crystals and needles, and that impurities favour the formation of needles, fibres and "amorphous" wax (*cf.* Ferris, Cowles and Henderson, *loc. cit.*). Branching of the chains also tends to cause the hydrocarbons to become amorphous. Dunmire[29] concludes that good rectification in vacuo is sufficient to produce a wax which crystallises well, the high-boiling colloid inhibitor of crystallisation being thereby

[24] *Ind. Eng. Chem.*, 1931, **23**, 681.
[25] *Nat. Petr. News*, 22.4.31, **23** (16), 49; 29.4.31, **23** (17), 67; 6.5.31, **23** (18), 51; 13.5.31, **23** (19), 71.
[26] *Erdöl und Teer*, 1931, **7**, 255, 270, 301.
[27] *J.I.P.T.*, 1930, **16**, 870.
[28] *Petr. Eng.*, Jan. 1931, **2** (4), 80.
[29] *Refiner*, May 1930, **9** (5), 136.

removed (*cf.* Sachanen etc., Bestushew *loc. cit.*, and Pyhala[30]). Paraffin crystals from low-temperature coal-tar have been shown by Tanaka, Kobayashi and Arakawa[31] to be similar in form and properties to those from petroleum and shale. Another study of the wax from low-temperature tar is that of Davis and Irey[32] who examined a high melting-point wax obtained from a Utah coal. This was found to consist mainly of pentacosane and heptacosane. They state that none of the true bituminous coals yield an appreciable quantity of wax.

Piper and Malkin,[33] continuing their work on the crystal structure of the normal paraffins, have shown that hexacosane and tetratriacontane show two stable forms at ordinary temperatures. The second, a newly observed form, occurs in even-numbered hydrocarbons with twenty-six or more carbon atoms. An X-ray diffraction study of wax by Clark and Smith[34] led to the conclusion that the material is composed of normal and iso-paraffins only, and that the diffraction method can be used to determine the proportions of these two types of compound which are present in a wax.

Papers by Carothers, Hill, Kirby and Jacobson[35] and Lander and Riedl[36] deal with the preparation of high molecular weight paraffin hydrocarbons.

Pyhala[37] has discussed the theoretical basis of the sweating process. He emphasises the need for rational temperature control and the desirability of forming large needle-shaped crystals. Similar points are brought out by von Groeling,[38] who advocates the cylindrical cell type of sweater.

An apparatus for continuous sweating is described by the Laboratory of Shell Group,[39] while Allan and Moore[40] and Allan[41] have patented new apparatus for sweating. A survey of the development of the sweating process and a description of the "Alanmor" stove is given by Allan.[42]

The cracking of Rangoon wax at 385° C. in an atmosphere of carbon dioxide has been studied by Waterman, Perquin and Van

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[30] *Erdöl und Teer*, 1931, **7**, 446.
[31] *J. Fac. Eng. Tokyo*, 1929, **18**, 109.
[32] *Ind. Eng. Chem.*, 1931, **23**, 186.
[33] *Nature*, 1930, **126**, 278.
[34] *Ind. Eng. Chem.*, 1931, **23**, 697.
[35] *J.A.C.S.*, 1930, **52**, 5279.
[36] *Coll. Czechoslav. Chem. Comm.*, 1930, **2**, 520.
[37] *Petr. Z.*, 1930, **26**, 115.
[38] *Petr. Z.*, 1930, **26**, 623.
[39] *Petr. Z.*, 1930, **26**, 1217.
[40] U.S.P. 1,743,746.
[41] E.P. 340,993.
[42] *J.I.P.T.*, 193 **7**, 657.

Westen,[43] and *in vacuo* by Heymans.[44] The latter showed that at 450° C. the splitting is much greater in the vapour than in the liquid phase. Unsaturated hydrocarbons are the principal products, at 700° C., the liquid products being almost entirely cracked.

Attention has been given by Wischnowitzer[45] to the problem of preparing odourless paraffin wax. He recommends treating the wax first with 66° Bé acid, followed by fuming sulphuric acid and sodium carbonate, and finishing by treatment with bleaching earth. A few papers have appeared dealing with the examination of waxes—*e.g.*, Dangl[46] suggests a method for the determination of melting-points by a microscopic method; while Piotrowski and Winkler[47] estimate the oil-content of waxes by a refractrometric method.

The composition of Montan wax has been investigated by Holde, Bleyberg and Vohrer in two papers.[48] The presence of acids with uneven numbers of carbon atoms could not be detected. A number of patents have been taken out to cover the preparation and purification of this wax.[49]

Solvents.

A noteworthy feature of the past few years has been the rapid rise in importance of industrial solvents derived from petroleum. Acetone, methyl, isopropyl, and amyl alcohols, ethylene glycol, acetates, chloro-compounds and hydrocarbons are manufactured in bulk, and represent a large and growing industry. A useful survey of the applications of these substances is given by Park.[50] Ethylene dichloride, dichlorethyl ether and isopropyl ether are dealt with by Fife and Reid.[51] The use of petroleum fractions and derivatives as diluents in the cellulose lacquer industry is also extensive. The use of naphthas is discussed by Brunkow,[52] by Durrans[53] in a general discussion on lacquer solvents and in an article[54] which deals with the substitution of toluole by V.M.P. naphtha. Ethylene dichloride is also dealt with by Frazier and Reid,[55] and secondary esters (acetates) by Park and Hopkins.[56]

[43] *J.I.P.T.*, 1930, **16**, 29.
[44] *J.I.P.T.*, 1930, **16**, 661.
[45] *Erdöl und Teer*, 1931, **7**, 142.
[46] *Petr. Z.*, 1931, **27**, 142.
[47] *Erdöl und Teer*, 1930, **6**, 463.
[48] *Brenn.-Chem.*, 1929, **10**, 105, 124.
[49] E.g., U.S.P. 1,737,975 and 1,767,886.
[50] *J.S.C.I.*, 1931, **50**, 620.
[51] *Ind. Eng. Chem.*, 1930, **22**, 513.
[52] *Ind. Eng. Chem.*, 1930, **22**, 177.
[53] *Oil and Colour Trades J.*, 1931, **79**, 177.
[54] *Oil and Colour Trades J.*, 1931, **79**, 1607.
[55] *Ind. Eng. Chem.*, 1930, **22**, 604.
[56] *Ind. Eng. Chem.*, 1930, **22**, 826.

Synthetic Products.

A very large number of compounds are now produced from petroleum, and find application either directly or as raw materials in some other branch of industry. Natural gas and cracking-plant gas are abundant sources of suitable compounds for use in this way. The hydration of olefines and the influence of pressure on the reaction is discussed by Swann, Snow and Keyes,[57] who used aqueous hydrobromic and hydriodic acid as catalysts. Ormandy and Craven[58] have investigated the action of sulphuric acid on olefines. Another paper in this field is that of Marcovitch and Moore[59], who investigated the absorption velocities of propylene, normal and iso-butylene and butadiene in sulphuric acid of various concentrations.

The addition of hydrochloric acid gas to olefines has received attention from Coffin, Sutherland and Maas,[60] who used the three butylenes in their investigation, and from Piotrowski and Winkler.[61] The latter investigators worked on the 20–40° C. fraction of cracked gasoline, and found that the optimum temperature for the addition was between 70° C. and 150° C. They recommend the use of contacting materials such as activated carbon or silica gel saturated with zinc or stannic chlorides. Several secondary and tertiary chlorides were isolated in good yield by fractionation.

Using partly reduced cupric chloride as a catalyst, Boswell and McLaughlin[62] obtained 80 per cent. yields of methyl chloride by chlorination of methane in a small apparatus.

Caproic acid has been prepared in yields up to 90 per cent. by Hass and Marshall[63] starting from amyl chloride and working through the nitrile.

Yoshikawa[64] studied the oxidation of methane at pressures up to 100 atms. and found formaldehyde and methyl alcohol among the products. Paraffin wax on oxidation gives acidic products, acquiring a saponification value of about 200 after a few hours air blowing at 170° C. in the presence of manganese and organic nitrogen compounds.[65] Swann, Howard and Reid[66] identified acetone, acetaldehyde, methyl and ethyl alcohols, acetic acid, allyl alochol and dimethyl acetal in the aqueous distillate from the oxidation of gas oil at 400° C. and 300 lb. pressure by the Penniman process.

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[57] *Ind. Eng. Chem.*, 1930, **22**, 1048.
[58] *J.I.P.T.*, 1931, **17**, 185.
[59] *Nat. Petr. News*, 14.10.31, **23** (41), 33; 21.10.31, **23** (42), 27.
[60] *Canad. J. Res.*, 1930, **2**, 267.
[61] *J.I.P.T.*, 1931, **17**, 225.
[62] *Canad. J. Res.*, 1929, **1**, 240.
[63] *Ind. Eng. Chem.*, 1931, **23**, 352.
[64] *Bull. Inst. Phys. Chem. Res. Japan*, 1931, **10**, 305.
[65] Hofmann, U.S.P. 1,762,688.

The oxidation of kerosine has been studied by Arditti,[67] who recognised acids, aldehydes, peroxides and unsaturated substances in the products. In spite of the extremely low price of natural rubber, the problem of producing this material synthetically continues to attract attention, mainly perhaps on political rather than economic grounds. A review of the situation is given by C. K. Francis.[68] A patent of Johnson and Carpmael[69] describes the preparation of rubber by the polymerisation of diolefines by sodium, in the presence of petroleum ether. An interesting study of the possibilities of producing a synthetic rubber starting from acetylene is contained in two papers from the du Pont laboratories.[70]

Acetylene is polymerised to vinylacetylene, and to this hydrogen chloride is added to give chloro-2-butadiene –1, 3 (" chloroprene ") which polymerises on standing to give rubber-like materials. The process appears to have distinct possibilities.

Miscellaneous Products.

Liquefied butane is now quite an important article of commerce in the U.S.A. Large quantities are transported in cylinders and tank-cars for use in industrial and domestic heating, welding, etc.[71]

Another product which has assumed great importance recently in America is carbon dioxide, which has an extensive use as a refrigerant under the name " dry ice." Large quantities of gas containing about 95 per cent. carbon dioxide and 5 per cent. of combustible gases are obtained from wells on the Quebrache oilfield. Pure solid carbon dioxide can be prepared from this gas and shipped for use as a refrigerant.[72] The Carbonic Products Co. treats 175,000 cub. ft. of natural gas, producing six tons of liquid and solid carbon dioxide, a day.[73]

A novel process is described by the Bayerische Metallwerke A.-G.,[74] in which metals and alloys of the tungsten-chromium or titanium groups are heated in a hydrocarbon-containing atmosphere to about 1500° C., when the resultant alloy, containing the hydrocarbon, possesses great sharpness and tensile strength.

Caplan[75] discusses the uses and properties of soluble cutting oils, and also the methods of manufacture.

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[67] *Ind. Eng. Chem.*, 1931, **23**, 1277.
[68] *Compt. rend.*, 1931, **193**, 589.
[69] *Oil and Gas J.*, 24.9.31, **30** (19), 24.
[69] E.P. 324,004.
[70] Nieuwland, Calcott, Downing and Carter, *J.A.C.S.*, 1931, **53**, 4197; Carothers, Williams, Collins and Kirby, *J.A.C.S.*, 1931, **53**, 4203.
[71] *Cf.* Kaye, *Petr. Eng.*, March 1931, **2** (6), 68.
[72] Martin, *Ind. Eng. Chem.*, 1931, **23**, 256; Sclater, *Petr. Eng.*, May 1931, **2** (8), 35.
[73] Staley, *Petr. Eng.*, Sept. 1931, **2** (13), 20.
[74] E.P. 316,103.
[75] *Petr. Eng.*, Nov. 1930, **2** (2), 95.

Several new emulsifying agents have been introduced recently. Prominent among these are trihydroxyethylamine stearate and ammonium linoleate. Both of these substances are useful in emulsifying oils for use as sprays, insecticides, etc., the emulsions thus prepared being of great stability.[76]

Published work on petrolatum seems to have been confined to patents for the preparation and purification of the material.[77] Some of these deal with the manufacture of white petrolatum, presumably for use in making cosmetics.

The utilisation of residues and by-products for power purposes was the subject of a paper by Dunstan at the Second Plenary Meeting of the World Power Conference at Berlin in June, 1930.[78] The recovery of acid from refining-sludge is discussed in an anonymous paper,[79] and the utilisation of by-products generally by Mekler.[80]

The manufacture of printers' inks affords another example of the minor uses of petroleum products, both oil and carbon black being employed in this material. Their composition and properties are discussed in a very interesting paper by Riddell,[81] who states that the presence of asphaltic matter, rather than the dark colour of the oils used, is responsible for the staining of the paper. Bowles[82] has also dealt with the problems involved in the use of printing inks.

[76] Bennett, *Ind. Eng. Chem.*, 1930, **22**, 1255.
[77] U.S.P. 1,733,597, 1,791,926, 1,785,270, etc.
[78] *J.I.P.T.*, 1930, **16**, 701; *Refiner*, July 1930, **9** (7), 125; Aug. 1930, **9** (8), 120.
[79] *Rev. Petr.*, 1930, (384), 1091.
[80] *Chem. and Met. Eng.*, 1931, **38**, 538.
[81] *Oil and Colour Trades J.*, 1931, **80**, 1472.
[82] *Oil and Colour Trades J.*, 1930, **78**, 1922.

Benzole.

By W. H. Coleman, F.I.C. (Member).

During the two years that have elapsed since writing the last article on Benzole very little of great interest has occurred. Perhaps the most outstanding event has been the publication of two books by the National Benzole Association—one "Specifications for Benzole and Allied Products," and the other "Motor Benzole: Its Production and Use," compiled by Messrs. Hoffert and Claxton, Research Chemists to the Association.

The use of benzole as a fuel for internal combustion engines has expanded both in this country and on the Continent of Europe, but it must not be forgotten that benzole, though an excellent motor fuel, is only produced in any quantity as a by-product of the high-temperature carbonisation of coal either at gas works or coke ovens, and consequently the quantity produced is limited.

Very little benzole is used alone as a motor fuel, but it is generally mixed with gasoline and sold as a blend in this country as "National Benzole Mixture," in Germany as "Aral," and in France as "Esbol."

Owing to the general world depression, the production of pig iron, and consequently that of metallurgical coke, has decreased, and so the production of benzole has fallen somewhat.

As mentioned two years ago, considerable research has been carried out on methods of refining benzole in order to avoid the loss due to the use of sulphuric acid.

Some of these processes were referred to before and during the period under review; their use has been extended and some new processes have been suggested. The process using ferric sulphate has been patented in America.[1]

T. Rabek[2] describes a process which is claimed to completely free benzole from thiophene. The same worker later condemns the sulphuric acid process of refining, as it removes unsaturated hydrocarbons, which, while having a good fuel value, have little tendency to form gum or resinous bodies. The Société du Gaz de Paris has taken out several patents.[3] Their process consists in passing the benzole, in the vapour phase, from the fractionating still through a column packed with porous material down which somewhat diluted sulphuric acid flows. It is claimed that only gum-forming hydrocarbons are removed and that the resulting benzole possesses good keeping qualities.

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[1] U.S.P. 1,742,343; *J.I.P.T.*, 1930, **16**, 114 A.
[2] *Brenn.-Chem.*, 1930, **11**, 189; *J.I.P.T.*, 1930, **16**, 262 A.
[3] E.P. 307,935, 314,052, 330,045; *J.I.P.T.*, 1930, **16**, 338 A.

R. C. Geddes[4] describes the use of silica gel as a refining agent, and claims that an increased yield of 13 per cent. is obtainable.

M. Kremer[5] advocates the use of anhydrous aluminium chloride for refining benzole, and states that the use of this material is much more advantageous than sulphuric acid.

The I.G. Farbenind A.-G. have patented[6] the use of maleic anhydride for refining benzole.

The above-mentioned processes, which do not include all the proposals that have been made, serve to show the interest that is being taken in obviating the losses consequent on sulphuric acid refining. The process of the National Benzole Association, mentioned two years ago, would save all losses on refining and so far is the most desirable. Large scale trials have been carried out over a lengthy period and have so far given satisfaction.

Work is being carried out on a test which will satisfactorily show whether a benzole, no matter what process of refining or stabilising has been adopted, will stand prolonged storage without developing gum or resinous bodies.

Reference must be made to the Active Carbon Process of recovering benzole from coal distillation gas and to the very valuable work of Mr. Hollins of the Gas Light & Coke Co., who has succeeded in so arranging the process that the life of the active carbon has been very considerably prolonged.

An interesting paper by Mr. S. Tweedy[7] gives figures showing the composition of benzole produced under various conditions of carbonising. From his remarks one gathers that the shorter the time of coking the higher the percentage of benzene results, and that prolonged time of coking and full charges result in increased proportions of paraffins.

This short article cannot be concluded without reference to a valuable contribution by F. H. Garner and E. B. Evans[8] on the estimation of corrosive sulphur in gasolines and benzoles. The spirit under test is refluxed with copper bronze powder for 1 to 1½ hours. The solid residue, after filtration, washing and drying, is dissolved in bromine water; hydrochloric acid is added, and the sulphur determined as barium sulphate. This method has been tested carefully and the results completely confirmed.

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[4] *Gas World*, 1931, **94**, Coking Sect., 17-20; *J.I.P.T.*, 1931, **17**, 78 A.
[5] *Petr. Z.*, 1931, **27**, 459-464; *J.I.P.T.*, 1931, **17**, 463 A.
[6] E.P. 352,164; *J.I.P.T.*, 1931, **17**, 464 A.
[7] *Gas World*, 1931, **94**, Coking Sect., 11-14; *J.I.P.T.*, 1931, **17**, 210 A.
[8] *J.I.P.T.*, 1931, **17**, 451.

Low-Temperature Carbonisation and Low-Temperature Tar.

By M. A. Matthews, D.Sc., Ph.D., F.I.C.

The year 1928 witnessed the maximum activity in the financial development of low-temperature carbonisation, and by 1929 forty-three companies had been registered in this country, representing a capital of eight millions sterling, with schemes proposed for dealing with the low-temperature carbonisation of two million tons of coal per annum. Owing to a number of causes, among which the industrial depression and technical difficulties encountered by the experimenters are prominent, few of these schemes have come to fruition, and in 1931 only about a quarter of a million tons of coal were carbonised at a low temperature.

The information which has been accumulated during the past few years directs attention to the fact that the economics of low-temperature carbonisation can only be considered in terms of the particular environment of each proposed plant. Mistakes in the choice of a suitable site have been made in the past[1] which are costly to rectify. No general principles can be laid down for the choice of a suitable environment, but all the factors must be taken into consideration. The chief factors which have to be borne in mind are briefly: the availability of the coal; the nature of the coal, which is preferably cheap, small coal of caking power suitable for the carbonising plant and also suitable for the production of satisfactory smokeless fuel; the disposal of the smokeless fuel, tar, liquor and gas. It is only in very exceptional circumstances that low-temperature carbonisation, by any process, can pay unless at least two of the three main products (coke, tar and gas) can be disposed of at prices considerably in excess, therm for therm, of that of the coal used. There seems little doubt that, given suitable conditions, more than one of the existing types of plant should be workable at a profit, although Tizard[2] has expressed the view that low-temperature carbonisation has now been given a full trial, and as an independent industry has proved to be a failure.

It should be remembered that low-temperature carbonisation of coal differs from the older established carbonisation industries in one important respect. The gas industry has gas as the main

[1] Col. W. A. Bristow, 14th Ann. Gen. Meeting of Low Temperature Carbonisation, Ltd.

[2] H. T. Tizard, British Association, London, 1931.

product and the coke-oven industry has coke as the main product, and both products can be sold at a figure calculated to yield a profit after credit has been taken for the by-products produced. With low-temperature carbonisation there is no main product that does not compete directly with other materials. For this reason one prospect for the development of low-temperature carbonisation is under the ægis of the gas industry. That this has been realised is evidenced in a paper by Milne Watson,[3] also by the fact that the Glasgow Corporation Gas Works is working the Maclaurin process and the South Metropolitan Gas Company has a "Coalite" plant at their Greenwich works. There is also a tendency to erect plants at collieries producing the type of coal required, in order to eliminate transport charges for coal, but the profitable disposal of the gas is then a problem.

An important development during 1930 was the formation of the Low-Temperature Distillers' Association of Great Britain. It is to be hoped that this association of the principal firms developing low-temperature carbonisation processes will assist in developments especially as regards the treatment and marketing of oils as well as in the general problems of preparing and marketing the smokeless fuel.

The experiment in low-temperature carbonisation conducted at the Richmond Gas Works by the Gas Light and Coke Company has now come to an end[4] and, chiefly owing to the short life of the metal retorts, the trial was not a success; but for many reasons the experiment is considered to be inconclusive.

Greatly improved results at higher throughputs have recently been obtained at the Fuel Research Station in a brick retort, and the fact that the Government is still convinced that the possibilities of low-temperature carbonisation are worth exploring is made evident by the arrangement for the development of low-temperature carbonisation at the Fuel Research Station to be conducted in conjunction with the hydrogenation of the tars produced.[4]

During the two years under review reports have been published by the Director of Fuel Research on tests carried out on the Babcock low-temperature carbonisation plant[5] at present in operation at the Dunston Power Station of the Newcastle Electric

[3] Sir D. Milne Watson, British Association, London, 1931.

[4] Report of the Fuel Research Board for the year ending March 31st, 1931, 2, 46, 52. H.M. Stationery Office. 2s. net.

[5] Report of Test by the Director of Fuel Research on "Babcock" Low-Temperature Carbonisation Plant installed by the Dunstan Power Station of the Newcastle-on-Tyne Electric Light Supply Co., Ltd., 1930. H.M. Stationery Office. 9d. net.

Light Supply Co., Ltd., the Bussey,[6] Turner[7] and L. and N.[8] low-temperature carbonisation plants. Fewer patents than in former years dealing with new, and improvements in the design of old, low-temperature carbonisation plants have been granted, but interest has recently been aroused in the Salerni process of carbonisation which has been described by Wheeler,[9] who states that "It is difficult not to conclude that by the Salerni system the admittedly difficult problem of low-temperature carbonisation of bituminous coals has been effectively solved."

General reviews of the present position of low-temperature carbonisation have been given by Lander[10] and Smythe[11]; Ormandy[12] considers the position of smokeless fuel from the national standpoint, while Berthelot[13] summarises the position of the technique of the low-temperature carbonisation industry in France, and stresses the importance of large carbonising units.

As previously mentioned, low-temperature tar has similar markets to those of the firmly established high-temperature tar products, and, although new uses for low-temperature tar may at any time be found,[14] its value at present is that of a crude fuel. For this reason opinion is inclining to the view that low-temperature tar must be looked upon as an intermediate product mainly to be converted by subsequent processes into more valuable products, *e.g.*, by hydrogenation into motor spirit or oils. The use of low-temperature tar as a fuel has been discussed by Hurley and Matthews,[15] and it is concluded that as a boiler fuel it is quite satisfactory if the necessity for mixing with petroleum oils does not arise. The tar oil distilled from the tar can be used in Diesel engines provided some means are provided to ensure its ready ignition. The conversion of low-temperature tar into motor spirit by hydrogenation is also dealt with in this paper, and by

[6] Report of Test by the Director of Fuel Research on a Retort of the Bussey Coal Distillation Co., Ltd., at Glenboig, Lanarkshire, 1931. H.M. Stationery Office. 9d. net.

[7] Report of Test by the Director of Fuel Research on the Turner Retort installed at the Comac Oil Co., Ltd., Coalburn, Lanarkshire, 1930. H.M. Stationery Office. 9d. net.

[8] Report of Test by the Director of Fuel Research on the Plant of the Leicestershire (L. & N.) Coal Distillation Co., Ltd., at Newbold, nr. Ashby-de-la-Zouch, 1931. H.M. Stationery Office. 9d. net.

[9] R. V. Wheeler, 3rd Int. Conf. on Bituminous Coal, Pittsburgh, 1931, **1**, 371.

[10] C. H. Lander, *Fuel Economy Review*, 1930, **9**, 19; 1931, **10**, 9.

[11] E. H. Smythe, *J.S.C.I.*, 1931, **50**, 588.

[12] W. R. Ormandy, *J. Inst. Fuel*, 1931, **5**, 56.

[13] M. C. Berthelot, *Ann. des Comb. Liq.*, 1930, **5**, 535.

[14] G. T. Morgan, *J.S.C.I.*, 1930, **49**, 249T; G. T. Morgan and N. J. L. Megson, *J.S.C.I.*, 1931, **50**, 191T.

[15] T. F. Hurley and M. A. Matthews, *J.S.C.I.*, 1931, **50**, 584.

Ormandy[12] and the Director of Fuel Research,[16] where it is shown that yields of 14 gals. of motor spirit can be obtained by hydrogenating 20 gals. of tar—the average yield obtained by the low-temperature carbonisation of 1 ton of bituminous coal.

The Admiralty has encouraged the production of fuel oil from coal by testing distillates from low-temperature tar. The Civil Lord of the Admiralty stated in the House of Commons on March 11, 1931, that of twelve samples tested, eight were quite satisfactory for use as Admiralty fuel oil.

The utilisation of low-temperature tar has been dealt with by Deville[17] who details the two methods which have been developed, namely, distillation and cracking. Cracking does not eliminate the tar acids, but only reduces their boiling point.[18] For economic reasons the installation of central refineries is advised.

A comprehensive study of the tars and oils produced from coal has been published by the Fuel Research Board.[19] This publication, which should be regarded as a reference work, summarises the present statistical and economic position of low-temperature tar, and contains an account of carbonisation experiments with three coals at temperatures from 400° to 700° C. by steps of 50° C., and at temperatures of 800° and 900° C. The work was undertaken mainly with a view to ascertaining the effect of temperature of carbonisation, and type of coal, on the nature of the tar produced; full carbonisation data are also given. The temperature of carbonisation at which the maximum tar production occurs with the system of carbonisation employed varies from 500° to 550° C. according to the type of coal used. Complete analyses of the twenty-seven tars produced are given and will serve as reference analyses with which other low-temperature tars may be compared.

The work on the identification of chemical compounds present in low-temperature tar has been continued by Morgan and his associates,[20] and the results of investigations carried out during the past five years at the Chemical Research Laboratory, Teddington, have been summarised.[21] A number of pure compounds have been isolated from low-temperature tar, including phenol and its homologues, pyridine and its homologues, quinoline and quinaldine, several methyl anthracenes and naphthalenes; and some of the

[16] Report of the Fuel Research Board for the year ending March 31st, 1930, 49, 111; 1931, 41. H.M. Stationery Office. 2s. net.

[17] J. St. C. Deville, *Ann. des Comb. Liq.*, 1931, **6**, 189.

[18] C. E. Senseman, *Ind. Eng. Chem.*, 1930, **22**, 81.

[19] Fuel Research Technical Paper No. 32, 1931. H.M. Stationery Office. 2s. net.

[20] G. T. Morgan and A. E. J. Pettet, *J.S.C.I.*, 1931, **50**, 72T; G. T. Morgan, F. S. Sinnatt and D. D. Pratt, E.P. 331,542 (1930); G. T. Morgan and D. D. Pratt, E.P. 327,797 (1930).

[21] G. T. Morgan, *Fuel*, 1931, **10**, 183.

simpler aliphatic acids have been isolated from low-temperature liquor. Morgan's researches have revealed the existence in low-temperature tar of neutral, basic, phenolic and acidic products of amorphous and resinous character which he has designated resinenes, resinamines, resinols and resinoic acids respectively.

The wax in low-temperature tar has been studied by Davis and Irey,[22] who find it consists mainly of pentacosane (m.p. 54° C.) and heptacosane (m.p. 60° C.), and its mode of crystallisation has been examined by Tanaka, Kobayashi and Arakawa.[23]

A method of determining the percentage of phenol in low-temperature tar has been described by Wiltshire,[24] who found as much as 1 per cent. to be present, whereas formerly there had been considerable doubt as to whether any phenol at all existed in low-temperature tar.

A number of patents have been taken out for the removal of tar acids from oils, *e.g.*, by extraction with triethanolamine[25] or from the low-boiling oils by cooling to below – 40° C.[26]

Low-temperature tar acids darken rapidly on standing; a phenomenon which has been shown to be due to the presence of polyhydric phenols.

The refining of tar acids by the preferential extraction of polyhydric phenols by borax, weakly alkaline buffer solutions and non-acidic salts of heavy metals has been patented,[27] while the refining of low-temperature tar and tar oils by treatment with sulphuric, hydrochloric, or phosphoric acids in methyl alcohol[28] has also been protected.

The refining with sulphuric acid of gas and tar spirits obtained by the low-temperature carbonisation of coal is recorded by Ruhermann[29] and by Hicks and King.[30] A water-white spirit can be obtained by refining with a suitable strength of sulphuric acid, but, although it remains colourless and does not deposit a gum on storage, the pre-formed gum increases. The spirits obtained from the low-temperature carbonisation of coal have a high H.U.C.R. (usually above 7 : 1, or a benzene – n. heptane equivalent of 75 : 25), but the anti-knock properties of these fuels decrease slightly on storage, the decrease being associated with the formation of peroxides.

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[22] J. D. Davis and K. M. Irey, *Ind. Eng. Chem.*, 1931, **23**, 186.
[23] Y. Tanaka, R. Kobayashi and I. Arakawa, *J. Fac. Eng. Tokyo*, 1929, **18**, 190.
[24] J. L. Wiltshire, *J.S.C.I.*, 1931, **50**, 125T.
[25] S. Metropolitan Gas Co. and H. Stanier, E.P. 344,614 (1931).
[26] I.C.I. Ltd., W. R. Madel and E. W. Fawcett, E.P. 355,212 (1931).
[27] S. Caplan, Assr. to Combustion Utilities Corp., U.S.P. 1,822,842 (1931); S. P. Burke, Assr. to Combustion Utilities Corp., U.S.P. 1,823,558 (1931); S. Caplan, U.S.P. 1,710,764 (1929).
[28] F. Hofmann and C. Wulff, E.P. 298,484 (1930); E.P. 301,420 (1930).
[29] S. Ruhemann, *Erdöl u. Teer*, 1931, **7**, 123.
[30] Fuel Research Technical Paper No. 34, 1931. H.M. Stationery Office. 6d. net.

Analysis and Testing.

By A. W. Cox, F.C.S. (Member).

Motor Spirit.

The physical and chemical examination of motor spirit continued to afford the most extensive field for study during 1930 and 1931. Much experimental work in test engines was carried out and efforts made to correlate analytical data to practical performance.

The outstanding features in the examination of spirits in testing engines are brought together in a Symposium presented at the annual meeting of the Society of Automotive Engineers in 1931.[1] This summarises the work done in this country and America, and deals with various designs of engines. The bouncing-pin continues to afford the best results for most purposes, and an engine (the C.F.R.) is brought practically to a standard in design.

H.U.C.R. is dropped in favour of the "Octane Number," which expresses the amount of iso-octane which can be added to normal heptane in order to obtain a spirit giving a resistance to knock equal to that of the sample under examination. Secondary standard fuels are made available in America to avoid the use of the expensive pure hydrocarbons. Consideration is given in the papers of this Symposium to the effect of variants on the knock-ratings obtained with standard fuels. These include air temperature, humidity, jacket temperature, cylinder head temperature, quantity of lubricating oil, carburettor setting, spark timing and sound intensity. Detailed instructions recommended for conducting knock-rating tests are given.

A large amount of other work on knock-ratings was done. It is shown[2] that, with a Pennsylvanian spirit, the fractions having lower densities and refractive indices had poorer knock-rating. Other workers,[3] using aniline as the anti-knock substance, show that in an homologous series of paraffin hydrocarbons the tendency to knock increases with increasing length of carbon chain, while in an isomeric series the tendency to knock decreases with addition of side chains. The introduction of the methyl group into a carbon chain decreases knocking tendency by about the same amount for each additional group. The same workers also investigated in a similar manner the olefine hydrocarbons,[4] and found that in an homologous series

[1] Detonation Symposium, Soc. Aut. Eng., 1931, or *S.A.E. Journal*, June, July and August, 1931.
[2] Fenske, *Ind. Eng. Chem.*, 1930, **22**, 913.
[3] Lovell, Campbell and Boyd, *Ind. Eng. Chem.*, 1931, **23**, 26.
[4] Lovell, Campbell and Boyd, *Ind. Eng. Chem.*, 1931, **23**, 555.

increasing length of carbon chain increased the tendency to knock, while in an isomeric series the knock decreased as the double bond became centralised. Further work by the same workers[5,6] is included in the S.A.E. Symposium.

Working on mixtures containing 20 per cent. of aromatic hydrocarbons in a standardised petroleum spirit and in comparison with a doped gasoline, it is shown[7] that the best anti-knock aromatics are meta and para xylenes and para cymene, and that in general the p-substituted benzenes are the best anti-knocks. In a further communication[8] the same workers, using a Delco unit, show that some unsaturated compounds have better anti-knock values than aromatics, but vary among themselves.

Other published work on engine tests[9,10,11] is included in the S.A.E. Symposium. It is suggested that engines at present in use may be calibrated against the C.F.R. unit, and it is pointed out that much yet remains to be done in this promising line of attacking the motor fuel question.

The tendency of cracked motor spirit to form gum is the basis of a number of investigations. Most incline to a more rapid method of evaporation than the I.P.T. Copper dish test, and advocate the use of glass instead of metal containers. A controlled current of air is recommended by several workers[12,13,14,15] for pre-formed gum. For the determination of the tendency to oxidise, it is suggested that cracked spirit is heated under pressure with oxygen,[14,16] but one worker found this method was attended with disastrous explosive results.[17]

Working with mixtures of 20 per cent. olefines in petroleum spirit, an investigator found that simple olefines do not produce gum when heated with oxygen for four hours at 100° C. at a pressure of 100 lbs./sq. in., but do so after twenty-four hours. Cracked spirit forms considerable gum under similar conditions, while diolefines form gum when evaporated in the normal manner.[99]

It is shown[18] that the darkening in colour of cracked spirit on ageing is not related to the amount of gum as usually determined,

[5] Boyd, *Ind. Eng. Chem.*, 1930, **22**, 1301.
[6] Campbell, Lovell and Boyd, *Oil and Gas J.*, 23.1.30, **28** (36), 42.
[7] Howes and Nash, *J.S.C.I.*, 1930, **49**, 16 T.
[8] Howes and Nash, *J.S.C.I.*, 1930, **49**, 113 T.
[9] *J.I.P.T.*, 1931, **17**, 69.
[10] Stacey, *Oil and Gas J.*, 5.2.31, **29** (38), 26.
[11] Sprake, *J.I.P.T.*, 1931, **17**, 471.
[12] *Rev. Petr.*, 1930, (362), 157.
[13] Littlejohn, Thomas and Thompson, *J.I.P.T.*, 1930, **16**, 684.
[14] Hann, Fischer and Blackwood, *J.S.A.E.*, 1929, **26**, 31.
[15] Bridgeman and Aldrich, *Oil and Gas J.*, 29.1.31, **29** (37), 42.
[16] Zublin, *Oil and Gas J.*, 16.7.31, **30** (9), 26.
[17] Francis, *Ind. Eng. Chem.*, 1930, **22**, 896.
[18] Brunschwig and Jacque, *Compt. rend.*, 1931, **191**, 1066.

and another investigator finds[19] that the oxidation of mercaptans is partly responsible for colour reversion. In the same paper the odour of cracked spirits is shown to be due to unsaturated compounds containing conjugated double-bonds, sulphur compounds, nitrogen compounds and secondary and tertiary alcohols formed by the action on olefinic compounds of the sulphuric acid used in refining.

A useful summary of the methods for estimating the various hydrocarbon series in motor spirits appeared[20], and further work[6] stated that unsaturated compounds are not removed quantitatively by potassium permanganate. Other investigators have also published work on the determination of olefinic and aromatic hydrocarbons,[21,22,23,24] the most interesting probably being a Report of the Department of Scientific and Industrial Research.[25] This Report concludes that results based on C.S.T. are inaccurate, and suggests that the aromatic content of spirit free from unsaturated compounds is determined by the use of 98 per cent. sulphuric acid to which is added 2 to 3 per cent. of silver sulphate. Naphthenes are estimated by reduction over heated palladium black and subsequent estimation of the aromatic compounds formed.

The relationship between engine performance and distillation test is the subject dealt with by several workers, chiefly in America. In one case[26] a relationship is shown between distillation, molecular weight and volatility, and several workers find that the 10 per cent. distillation point is of great value in judging the value of a spirit.[27] One report[28] includes a table which shows the A.S.T.M. distillation results needed, under various atmospheric conditions, in two kinds of engine, in order to obtain maximum general efficiency. Another paper[29] records that the 10 per cent. A.S.T.M. distillation point should not greatly exceed 60° C. if easy starting at 0° F. is desired and it is pointed out that differences in End Point between 185° C. and 230° C. have little effect either on starting up or on general performance. Another worker considers that the 30 and 65 per cent. points are a satisfactory indication of volatility.[30]

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[19] Burrell, *Nat. Petr. News*, 12.3.30, **22** (11), 57.
[20] Howes, *J.I.P.T.*, 1930, **16**, 54.
[21] Faragher, Morrell and Levine, *Ind. Eng. Chem., Anal. Ed.*, 1930, **2**, 18.
[22] Davie and Quiggle, *Ind. Eng. Chem., Anal Ed.*, 1930, **2**, 39.
[23] Mocklich and Conrad, *Z. angew. Chem.*, 1930, 488.
[24] Towne, *J.I.P.T.*, 1931, **17**, 134.
[25] Manning and Shepherd, Dept. Sci. Ind. Res., Fuel Res., *Tech. Paper No.* 28.
[26] Brown and Skinner, *Ind. Eng. Chem.*, 1930, **22**, 278.
[27] Moore and Reynolds, *Proc. Amer. Petr. Inst.*, 1930, **11**, 39.
[28] *Ind. Eng. Chem.*, 1930, **22**, 649.
[29] Burrell, *Nat. Petr. News*, 26.3.30, **22** (13), 72.
[30] Zublin, *Nat. Petr. News*, 21.5.30, **22** (21), 40.

Vapour lock is a question which has assumed greater importance since the more extensive use of casinghead gasoline in gasoline blends. One paper indicates that Vapour Pressures accurate to 0·2 lbs./sq. in. can be predicted from the A.S.T.M. distillation results.[31] Further studies on dew point, equilibrium volatility, distillation and vapour pressure and the correlation of engine results with A.S.T.M. distillation figures are recorded in a Michigan Bulletin.[32]

Several modifications in the lamp method of sulphur estimation have been proposed. One proposal[33] is that very light distillates should be kept in an ice-water bath. Another[34] puts forward ideas for adjusting the height of flame, improving absorption and avoiding blank determinations, while yet a further suggestion[35] is the assisting of the burning of the lamp by passing an air current through an annular space surrounding the tube in which the flame is burning.

Working on other lines, English workers[36] suggest the estimation of corrosive sulphur in motor spirits by boiling with copper-bronze, and subsequent estimation as barium sulphate by a modification of the I.P.T. method. From these experiments, it is concluded that a spirit containing up to 0·5 mg. free sulphur per 100 ml. is non-corrosive, up to 1 mg. is fairly good, and above 1 mg. is likely to cause serious trouble. In this connection one notes a modified Doctor Test by the Natural Gasoline Association of America.[37]

Two workers point out[38, 39] the inadequacy of the usual sulphuric acid test for motor benzole, and one suggests[39] the rapid evaporation of the benzole in a current of air and the examination of the residue, which should not exceed 10 mg. per 200 ml.

The calculation of the vapour pressure of toluene forms the subject of an interesting investigation.[40] A paper on the decomposition of hydrocarbons by heat,[41] while mainly useful from a pyrogenetic point of view, is also valuable from an analytical standpoint.

Methods of estimation of lead tetraethyl include one using bromine[42] and one[43] acetyl chloride for the decomposition of the

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[31] Bridgeman, Aldrich and White, *Proc. Amer. Petr. Inst.*, 1930, **11**, 4.
[32] Dept. Eng. Res., Mich. Univ., *Bull.* 14, 1930.
[33] Wood and Mattox, *Ind. Eng. Chem., Anal. Ed.*, 1930, **2**, 24.
[34] Edgar and Calingaert, *Ind. Eng. Chem., Anal. Ed.*, 1930, **2**, 104.
[35] Formanek, *Chem. Z.*, 55, 531.
[36] Garner and Evans, *J.I.P.T.*, 1931, **17**, 451.
[37] *Oil and Gas J.*, 1.1.31, **29** (33), 105.
[38] Rabek, *Brenn-Chem.*, 1930, **11**, 189.
[39] Knottner, *Brenn-Chem.*, 1930, **11**, 432.
[40] Davis, *Ind. Eng. Chem.*, 1930, **22**, 380.
[41] Dunstan, Hague and Wheeler, *J.S.C.I.*, 1930, **50**, 313 T.
[42] Catlin and Starrett, *Chem.-Anal.*, 1930, **19** (5), 5.
[43] Weiss, *Petr. Z.*, 1931, **27**, 113.

lead compound, the former estimating by titration and the latter gravimetrically as lead sulphate.

The use of sodium-potassium alloy is suggested for the determination of water in motor spirits,[44] the resulting hydrogen being separated by freezing the spirit in liquid air. It was thus found that five aviation spirits examined gave a maximum water content of 0·013 per cent. The action of magnesium nitride with subsequent recovery of ammonia is used for the estimation of water in alcohol fuels in one investigation.[45]

A considerable amount of work on molecular weights, specific heats, refractive indices and co-efficients of expansion is recorded in two papers.[46, 47]

Work on pure hydrocarbons includes a paper on the density of gaseous propylene[48] and the oxidation of methane by copper oxide[49, 50]. The latter shows that oxidation is slow up to 700° C. and rapid above that temperature, but that the addition of cuprous chloride renders oxidation rapid below 430° C.

Kerosine.

The effect of the composition of kerosine on its illuminating power is investigated,[51] and it is concluded that olefines tend to decrease the illuminating power, while aromatic compounds increase the amount of light up to a certain point which varies with the oil and the lamp.

Other work relates tendency to smoke to composition, using the lamp from a Weber photometer,[52] and shows that the tendency to smoke is directly proportional to the aromatic and naphthenic content over a given range of boiling points. Molecular complexity causes increase in smoking.

Two patents deal with the question of colour matching. One[53] uses a photo-electric cell with tri-chromatic colorimeter and the other varying amounts of red, green and blue colours.[54]

Lubricating Oil.

The work of the Department of Scientific and Industrial Research on lubrication continues to afford valuable information. By working

[44] Aldrich, *Ind. Eng. Chem., Anal. Ed.*, 1931, **3**, 348.
[45] Dietrich, *Erdol and Teer*, 1931, **7**, 317.
[46] Lang, Jessel and Steed, *J.I.P.T.*, 1930, **16**, 783.
[47] Lang and Jessel, *J.I.P.T.*, 1931, **17**, 572.
[48] Ormandy & Craven, *J.S.C.I.*, 1930, **49**, 374 T.
[49] Campbell and Gray, *J.S.C.I.*, 1930, **49**, 432 T.
[50] Campbell and Gray, *J.S.C.I.*, 1930, **49**, 447 T.
[51] Danaila, Stoenescu and Dinescu, *Petr. Z.*, 1930, **26**, 47.
[52] Minchin, *J.I.P.T.*, 1931, **17**, 102.
[53] Hilgar, E.P. 324,351.
[54] Houston, E.P. 324,495.

with a "normal" liquid, such as medicinal paraffin, in admixture with various proportions of paraffin wax and palmitic acid, it is shown that lubricating oils contain an active constituent which can be removed by extraction with acetone or adsorption on glass or silica. The effect of mixtures of the "medium" with active constituents is demonstrated.[55]

Later work, details of which are not yet published, deals with lubrication and frictional resistance. The falling sphere method of testing is favoured for rapid determinations of viscosity, and apparatus for this purpose is being elaborated.[56]

The cryoscopic determination of the molecular weights of lubricating oils using benzene as solvent is dealt with in detail,[57] and in the case of Pennsylvanian oils a direct relationship is found to exist between molecular weight and specific gravity, refractive index, absolute viscosity, and flash point. Somewhat similar results are recorded by other workers in America.[58]

Work on viscosity includes methods of calculating viscosities at temperatures other than those of the determination[59, 60] and the calculation of viscosities of mixtures.[60] The comparison between the Echart logarithmic relation and Redwood and absolute viscosities is considered, and it is found that, while a fair relationship exists, the constants vary with different oils.[61]

An article[62] gives a table of absolute viscosities derived from Engler degrees, and it is found that above 8° Engler the absolute viscosity can be calculated from the formula $\eta = 7{\cdot}6\ E°$.

New forms of lubricating oil viscometers include a pipette viscometer which uses 25 ml. of oil and can be calibrated against the Redwood instrument[63] and a modification of the Engler viscometer for direct determination of viscosity in c.g.s. units.[64]

An excellent book on viscometry has been published[65] and deals with commercial as well as more scientific methods of viscosity determination.

The estimation of acidity by electrometric methods has received further attention, and it has been found[66] that silver silver-chloride

[55] Dep. Sci. Ind. Res., Lub. Res., *Tech Paper No.* 1.
[56] Dep. Sci. Ind. Res., Report, 1930/31.
[57] Gullick, *J.I.P.T.*, 1931, **17**, 541.
[58] Davis and McAllister, *Ind. Eng. Chem.*, 1930, **22**, 1326.
[59] Sloane and Winny, *Ind. Eng. Chem.*, 1931, **23**, 673.
[60] Walther, *Petr. Z.*, 1930, **26**, 755.
[61] Baillie, *J.I.P.T.*, 1930, **16**, 643.
[62] *Petroleum*, 1930, **26**; *Motor*, **3**, 3.
[63] Romney, *J.S.C.I.*, 1930, **49**, 986.
[64] Schaffer, *Petroleum*, 1930, **26**; *Motor*, **3**, 4.
[65] Barr, "A Monograph of Viscometry."
[66] Seltz and Silverman, *Ind. Eng. Chem., Anal. Ed.*, 1930, **2**, 1.

electrodes are easier to prepare than the previously suggested quinhydrone electrodes[67] and give accurate results when butyl alcohol is used as solvent.

It is claimed[68] that a breakdown test involving heating to 150° C. for 30 hours with shaking so as to expose fresh surfaces to the air causes an alteration in lubricating oil similar to that which occurs after 150 hours use in an engine.

Transformer Oils.

The question of sludge formation in insulating oils has been investigated by several workers. It is found[69] that metals which increase acidity in oil also increase the amount of sludge formed. With a highly refined oil it is found that lead. iron, zinc and magnesium tend to reduce acidity and sludge, while with a less completely refined oil copper, brass, silver and lead increase sludge formation and magnesium, tin, aluminium and zinc decrease the amount.

The same workers[70] deal with the effect of various metallic soaps of naphthenic acids in poorly refined switch oils. They find that the soaps of copper, iron, manganese, silver, cobalt and cerium cause increase in sludge, whereas those of calcium, barium, mercury, potassium, magnesium and tin cause a decrease. The tin soap when present to the extent of 0·1 per cent. inhibits the formation of sludge and does not reduce breakdown voltage more than 0·1 per cent.

Another paper records[71] that the presence of sulphur and unsaturated compounds are necessary to the formation of sludge. Previous work is confirmed and extended in a paper[72] showing that the direct cause of sludge formation and change of colour in insulating oils is the presence of oxygen. When heated for 100 hours at 140° F. in a vacuum or in a closed space filled with nitrogen, carbon dioxide or hydrogen, no change in colour or formation of sludge is found to occur.

It is claimed[73] that by heating transformer oil at 120° C. for 100 minutes with oxygen in the presence of silica gel and ferric oxide an effect is produced on the oil similar to that which would occur during one year in service. In a previous paper[74] calculations of saponification value, acid value and tendency to polymerise

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[67] Seltz and McKinney, *Ind. Eng. Chem.*, 1928, **20**, 542.
[68] Damian and Dixmier, *Chim. et Ind.*, **23**, 834.
[69] *J.S.C.I., Japan*, 1930, **33**, 113.
[70] *J.S.C.I., Japan*, 1930, **33**, 318.
[71] Mizushima and Yamada, *Res. Elec. Tech. Lab., Tokio, No.* 291.
[72] Yamada, *J.S.C.I., Japan*, 1930, **33**, 64 B.
[73] Evers, *Z. angew. Chem.*, 44, 323.
[74] Evers and Schmidt, *Wiss. Ver. Siemens-Konz.*, 9 (1), 357.

are made from the "ageing value" as determined above, and thus an estimate is made of the probable length of life of the oil under electrical conditions.

The acidity in transformer oils is found to be accurately determined by the potentiometric method mentioned above,[66,67] but it is considered too lengthy for commercial practice.[75] The use of alkali blue as indicator in the A.S.T.M. method for acidity is recommended in the same communication.

Fuel Oil.

The determination of sulphur content by the bomb method is found to be more accurate in a bomb lined with vitreosil than with a gold or platinum lining,[76] the calorific value being unaffected by this alteration. Other investigators recommend that a few crystals of ammonium nitrate be placed in the bomb capsule when determinations of sulphur content are made.[77] A description is published of a new apparatus for the determination of the spontaneous ignition temperature of fuel oil.[78]

Bitumen, Tar, Asphalt.

An investigator determines the value of a tar as a road material by microscopic examination of the contained carbon microns.[79] Glycerine is recommended as the bath liquid in the determination of melting point, ductility and float test,[80] as it is found that the presence of water or water vapour is likely to upset the results.

An interesting suggestion for the determination of melting point is made[81] in which the substance is placed along a copper bar which is heated electrically to different temperatures along its length. It is readily seen at which point on the bar the sample melts, and the temperature at that point is taken by potentiometric measurement.

A method for the estimation of wax in petroleum residues (road asphalt) involving the distillation of ten grams of substance and precipitation by means of acetone of the wax distilled over has been worked out in detail.[82]

The separation of mineral bitumen from coal tar or brown coal tar mixtures by sulphonation and subsequent differences in solubility in water is recommended in one communication.[83] Mineral bitumen under this treatment is found to remain insoluble.

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[75] Evans and Davenport, *Ind. Eng. Chem., Anal. Ed.*, 1931, **3**, 82.
[76] Bates, *Ind. Eng. Chem., Anal. Ed.*, 1930, **2**, 162.
[77] Garelli and Saladini, *Ann. Chim. Appl.*, 21, 136.
[78] Dunkerley, *Petr. Times*, 1931, 25, 389.
[79] Loman, *Roads and Road Constr.*, 1930, **8**, 45.
[80] Eisner, *Petr. Zeit.*, 1930, **26**, 13.
[81] Dennis and Shelton, *J.A.C.S.*, 1930, **52**, 3128.
[82] Littlejohn and Thomas, *J.I.P.T.*, 1930, **16**, 814.
[83] Marcusson and Lederer, *Petr. Z.*, 1930, **26**, 866.

A falling sphere viscometer, in which the falling of the sphere is determined by electrical methods, is recommended as being more reliable and quicker for testing tar than the usual instruments.[84]

Interesting research to obtain information as to the natural weathering of road asphalt shows that exposure to arc lamp radiation, chilling, and spraying with water give a similar effect in a short time to that which occurs in actual use over a long period.[85]

The British Standards Institution published in 1931 specifications for Cold Asphalt Macadam (No. 433) and Asphaltic Bitumen Road Emulsion (No. 434).

Lubricating Grease.

A method for the estimation of glycerol in grease is devised[86] in which the carbon dioxide formed by the action of chromic acid on the glycerol is absorbed and estimated.

A consistometer for greases in which grease is caused to flow through a capillary under a head of mercury is claimed to give an accuracy of 2 per cent.[87]

Miscellaneous.

The relationships between specific and total heats and other properties of petroleum fractions has been tabulated.[47] Measurements of the compressibilities and co-efficients of expansion of fourteen samples of petroleum oils have been determined at temperatures from 0 to 30° C. and at pressures up to 50 kg./sq. cm.[88] These figures are then correlated to viscosity.

An apparatus for the extraction of one liquid by another is noted for its simplicity.[89]

The A.S.T.M. published their annual Reports of Committee D–2 in 1930 and 1931, giving their latest methods of petroleum testing.

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[84] Broome and Thomas, *J S C.I.*, 1931, **50**, 424 T.
[85] Strieter, *Bur. Stand. J. Res.*, 1930, **5**, 247.
[86] Pramme, *Ind. Eng. Chem., Anal. Ed.*, 1931, **3**, 232.
[87] Bulkley and Bitner, *J. Rheo.*, 1, 269.
[88] *Bur. Stand. J. Res.*, 1930, **5**, 985.
[89] Forster, *J.S.C.I.*, 1931, **50**, 44.

Chemistry of Petroleum.

By H. I. Waterman (Member), A. J. Tulleners (Student Member) and W. C. Webber, M.A. (Assoc. Member).

The lines of demarkation between the chemical and the petroleum industries are rapidly becoming less distinct. No better indication of this tendency for the two industries to become merged could be found than from a consideration of the trend of the investigations which have been conducted during the last two years and their commercial application.

The synthesis of alkylchlorides and alcohols from paraffins and unsaturated compounds is a good example of the manner in which an offshoot of the petroleum industry has linked itself up with the manufacture of such products as artificial silk, lacquers and refrigerants through the development of organic solvents from light petroleum hydrocarbons. Lee H. Clark[1] describes the evolution of this new chemical industry and gives an account of a plant for the synthesis of amylchlorides and amylalcohol from the pentanes by direct chlorination.

The promise given by this particular line of research is well illustrated by the work of W. J. Piotrowski and J. Winkler[2] on the catalytic addition of hydrogen chloride to unsaturated hydrocarbons. These investigators using that likely material, cracked gasoline, produced by one of the so-called "liquid phase" processes, obtained quantitative yields of secondary and tertiary alkylchlorides through the catalytic action of various metal chlorides. They found the best yields were given by the polychlorides of the heavy metals deposited on activated carbon, or silica gel, between temperatures of 70°–150° C. Zinc and stannic chlorides were particularly effective catalysts, but sulphur compounds gradually "poison" the contacting mass, and these therefore must be removed.

Mention must also be made of the work of H. B. Haas and J. R. Marshall,[3] who, starting with natural gas, worked out a process for the synthesis of caproic acid from natural gas by hydrolyzing amylcyanide produced in good yield from the chloride. Caproic acid finds application pharmaceutically in the preparation of hexylresorcinol.

A definite step nearer the realization of satisfactory synthetic rubber, towards which progress has been slow since the search received its initial fillip in Germany during the Great War, has

[1] *Chem. Met. Eng.*, 1931, **38**, 206.
[2] *J.I.P.T.*, 1931, **17**, 225.
[3] *Ind. Eng. Chem.*, 1931, **23**, 352.

now been taken as a result of J. A. Nieuwland's and W. H. Carothers' excellent work on the polymerization of acetylene.

Using aqueous cuprous chloride as a catalyst, the former[4] describes a low temperature polymerization of acetylene to vinylacetylene, divinylacetylene and a tetramer, the properties of which are given. Carothers and his collaborators [5] have prepared chloroprene by the catolytic addition of hydrogen chloride to vinylacetylene. In aqueous emulsion they found that chloroprene rapidly polymerizes into μ-polychloroprene, which is a synthetic (vulcanized) latex of a much finer state of dispersion than natural latex. Consequently it penetrates materials more readily. Chloroprene can thus be polymerized in the pores of a porous or absorptive material, impregnating it with synthetic rubber. Compared with natural rubber the new product is reported as more dense, more resistant to the action of water, petroleum hydrocarbons and less permeable to gases. It is also claimed to be more resistant to attack by oxygen, ozone, hydrogenhalides and many other chemicals.

Again, in another direction, one of the outstanding recent discoveries has been "Paraflow," which is finding important industrial application for reducing the pourpoint of paraffin base oils. "Paraflow" is a pure hydrocarbon lubricant and is said to consist essentially of a condensation product of 125° C.M.P. paraffin with naphthalene fully chlorinated at 200° F.[6] Small quantities only of "Paraflow" are required, and it has no deleterious effect on other desirable properties of the luboil.

The Chemistry of Cracking.

The mechanism of cracking reactions is still receiving a good deal of attention, and explanatory theories are now taking on a more definite shape. The theory that cracking proceeds in progressive stages *via* the production of free radicals now seems to be receiving general support, largely as a result of work done on the pyrolysis of hydrocarbon gases. Particularly noteworthy in this connection has been the work of R. V. Wheeler on the thermal decomposition of methane. This investigator, with W. L. Wood,[7] made "stream" experiments in which large volumes of methane were passed through heated tubes composed of different materials, the liquid and gaseous products of decomposition being collected and analysed. "Static" experiments were also conducted, in which the methane was heated in a quartz bulb at different temperatures, pressure changes being recorded by a manometer. It

[4] *J.A.C.S.*, 1931, **53**, 4197.
[5] *J.A.C.S.*, 1931, **53**, 4203.
[6] Davis and Blackwood, *Ind. Eng. Chem.*, 1931, **23**, 1452.
[7] *Fuel*, 1930, **9**, 567.

was found a temperature of 650° to 675° C. was required to decompose methane, even in the presence of catalysts known to accelerate decomposition at higher temperatures. It was demonstrated that the breaking up of the methane could not be represented by the simple equation $CH_4 \rightarrow C+2H_2$, since small amounts of tars and ethylene were also formed.

In the "stream" experiments with a heating period of about 0·3 secs. at 1050° C. and using a silica tube, 84 per cent. of the methane split up and formed higher hydrocarbons, among which butylene and butadiene were detected, but no propylene or acetylene. The authors explain their results by the successive decomposition of the methane into the free radicals methyl, CH_3, methylene, CH_2, and methine, CH. Some of these free radicals instead of decomposing further, are held to inter-react with the production of ethane, ethylene, acetylene, etc. Further reactions of these molecules containing two carbon atoms lead to the formation of higher hydrocarbons including aromatics. Ethane itself does not take a direct part in the formation of aromatic hydrocarbons, but first breaks up into ethylene and hydrogen.

T. S. Wheeler,[8] surveying the experimental evidence available on the kinetics of the decomposition of methane, concluded that in the presence of silica, porcelain and chrome iron the reaction was heterogeneous and retarded by the hydrogen produced. An equation is derived, fitting the experimental results, indicating the rate of decomposition to be a function of both the hydrogen and methane concentrations.

The pyrolysis of ethylene has been studied by H. I. Waterman and A. J. Tulleners [9] under high pressure in a steel autoclave. They found decomposition took place at 375° C. with explosive violence to carbon, hydrogen and methane.

E. Berl and W. Forst [10] also investigated the cracking of ethylene, and have obtained yields of 40 per cent. liquid products at temperatures between 800° and 900° C. They demonstrated the catalytic effect of metals and metallic oxides in preventing the formation of liquids and in favouring the production of the free elements. Benzene, naphthalene and anthracene formed the chief constituents of the liquid portion, cyclopentadiene being also indentified. The authors consider the evidence entirely accords with the theory that these liquid hydrocarbons were built up from the free radicals released as a result of the breaking up of the ethylene molecule. These radicals, they hold, are either hydrogenated to gaseous products, or polymerized to liquid and solid compounds.

[8] *Fuel*, 1931, **10**, 175.
[9] *J.I.P.T.*, 1931, **17**, 500.
[10] *Z. angew Chem.*, 1931, **44**, 193.

The same authors also studied the pyrolysis and polymerization of acetylene, and found almost a complete conversion to aromatic liquids at 740° C., the yield being favourably influenced by the presence of water.

C. D. Hurd and R. N. Meinert[11] have similarly studied the pyrolysis of propylene, which they found was rapidly decomposed at temperatures above 600° C. in pyrex or quartz. The gaseous products were largely hydrogen, methane and ethylene, with smaller amounts of acetylene and ethane. Aromatic liquids (benzene, toluene, etc.) comprised approximately 25 per cent. of the total reaction products. The reaction was shown to be predominantly homogeneous and unimolecular.

Under comparable conditions, propylene was found to decompose at a much lower temperature—namely, 350° C.—the products being mainly carbon and hydrogen. The mode of decomposition of propylene was shown to be practically identical with that of isobutylene.

The pyrolysis, both catalysed and uncatalysed, of propane has been investigated by G. O. Ebrey and C. J. Engelder,[12] who found that the principal products were hydrogen, methane, ethylene, propylene and ethane up to a temperature of intensive decomposition; whilst of special interest is the observation of K. Frolich, R. Simard and A. White,[13] who produced 20·6 mols. of butadiene for every 100 mols. of cyclohexane decomposed by cracking in quartz tubes at 654° C.

There is next the contribution of H. T. Waterman, J. N. J. Perquin and H. A. van Westen[14] on the pyrogenetic disruption of paraffin wax under atmospheric pressure and at low temperature (360° C.). These authors proved the decomposition takes place in accordance with the scheme of Haber, small saturated fragments being first broken off at the ends of the paraffin molecules, together with traces of hydrogen. After a short time, however, the course of the reaction becomes complicated by secondary changes, due to olefins of high molecular weight becoming less unwieldy in size by shedding ethylene, propylene, etc.

The experimental results on the mechanism of the cracking reaction are after all what might be expected, theoretically, from a consideration of the strengths of the atomic linkages involved.

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[11] *J.A.C.S.*, 1930, **52**, 4978.

[12] *Ind. Eng. Chem.*, 1931, **23**, 1033.

[13] *Ind. Eng. Chem.*, 1930, **22**, 240.

[14] *J.I.P.T.*, 1930, **16**, 29.

When subjected to heat stress the molecule naturally breaks at the weakest link which, as pointed out by F. O. Rice,[15] is usually at a linkage. A bond (93·3 kg. cal.) is stronger than a (71·0 kg. cal.), as is also the double bonded linkage=C=C=. Once broken off, the free radicals are at liberty to polymerize, inter-react, mainly forming aromatic hydrocarbons, or alternatively to decompose further. It is to be expected, therefore, that in all these processes the reaction products should to a certain extent be independent of the nature of the raw material. Strength is lent to this view by the researches of E. Berl and W. Forst[16] on the pyrolysis of paraffin wax and paraffin oil. The aromatic reaction products they produced, consisting chiefly of benzene, naphthalene and anthracene, with cyclic compounds containing side chains to a minor extent, are similar to those obtained from acetylene and ethylene.

Finally, a brief review of the progress made in this section would not be complete without reference to J. F. Norris and G. Thomson's[17] experiments on the influence of temperature on the velocity of decomposition of hydrocarbons. These investigators showed that for each compound tested, namely, n-pentane, isopentane, pentene 1, pentene 2 and trimethylethylene the rate of increase is constant per degree rise in temperature, within certain temperature limits, above which the velocity increases more rapidly. Traces of moisture have no effect on the cracking of pentene 2, but doubles the rate of decomposition. The authors observed on heating up olefins, a temperature was reached at which no further expansion took place. The results indicated that this is the point at which the expansion due to cracking becomes equal to the contraction due to polymerization. The reverse process

Polymerization has also been an attractive subject for investigators, particularly with ethylene, and mainly in connection with the manufacture of synthetic lubricating oils. H. I. Waterman and A. J. Tulleners[18] investigated the decomposition of ethylene at various temperatures under normal pressure, in the absence of catalysts. Employing a "once through" system, they obtained at a temperature of 700° C. a yield of 12·8 per cent. by weight of a light distillate, rich in benzene, boiling up to 150° C. and 17·4 per cent. of tar. Under these conditions practically no carbon was formed

[15] *J.A.C.S.*, 1931, **53**, 1959.
[16] *Z. angew Chem.*, 1931, **44**, 833.
[17] *J.A.C.S.*, 1931, **53**, 3108.
[18] *Brenn.-Chem*, 1930, **11**, 337

(0·35 per cent.). The yield of oil and tar was higher at 800° C., but the carbon percentage was also increased to 2·8 per cent.

The rate of polymerization of ethylene has been measured by R. N. Pease [19] at 2·5, 5 and 10 atmospheres at temperatures between 350° and 500° C. Under these conditions at least 50 per cent. of the ethylene could be polymerized to gaseous and liquid mono-olefins without the simultaneous formation of more than a few per cent. of hydrogen and saturated hydrocarbons. The reaction is of the second order and has an abnormally low temperature coefficient.

Interesting results were obtained by A. W. Nash, H. M. Stanley and A. R. Bowen [20] in synthesising lubricating oils from ethylene under pressure, using freshly sublimed $AlCl_3$ as a catalyst. Lacking a catalyst, ethylene was found to require a minimum temperature of 325° C. for polmerization, but this temperature was lowered by $ZnCl_2$, $SnCl_4$ or $TiCl_4$, $AlCl_3$ being particularly active. The reaction was found to be of the Friedel-Crafts type. The oils produced contained a whole range of hydrocarbons, from gasoline to heavy lubricating oil fractions. At temperatures between 0–20° C. the reaction products consisted of a comparatively saturated, uncombined and colourless oil made up of hydrocarbons of the type C_nH_{2n}, and also a pasty double compound of $AlCl_3$ which was readily decomposed by water to release a darker coloured oil containing a mixture of hydrocarbons of the types C_nH_{2n} and C_nH_{2n-2}. Extending the period of contact of the reactants did not increase the yield of oil obtained from the double compound, whilst rising temperature augmented the production of the free oil and increased its volatility. At 150° C. only a highly carbonaceous residue could be obtained by the action of water on the double compound. These synthetic luboils were inferior to petroleum lubricants as regards susceptibility to oxidation and viscosity.

F. W. Sullivan, Jr., V. Voorhees, D. W. Neeley and R. V. Shankland [21] also investigated the properties of the luboil fractions contained in the reaction products produced by the polymerization of olefins and cracked distillates in the presence of aluminium chloride. They established that the viscosity index of the luboil increases with the molecular weight of the olefin used as raw material.

Chemistry of High Pressure Hydrogenation.

In keeping with the rapid industrial development of high pressure hydrogenation, the amount of experimental work has greatly

[19] *J.A.C.S.*, 1931, **53**, 619.
[20] *J.I.P.T.*, 1930, **16**, 830.
[21] *Ind. Eng. Chem.*, 1931, **23**, 604.

increased. This is particularly the case as regards the use of hydrogenation for refining purposes, where it has special importance in view of the possibility of preparing special products by the flexibility of the process, and the easy elimination of all forms of sulphur by using the right catalyst.

Among the major applications of catalytic high pressure hydrogenation may be mentioned [22]:—

1. The conversion of heavy asphaltic crude oils and residues into gasoline and distillates.
2. The production of lubricating oils with flat temperature-viscosity curves.
3. The refining of inferior burning oil distillates.
4. The conversion of paraffinic gas oils into low sulphur gasolines of good anti-knock quality, without the formation of coke or heavy by-products.

The researches of Haslam and Russell and their collaborators have thrown considerable light on this subject, especially as regards the use of poison-free catalysts.

Anything more than the briefest of references on the purely chemical side of hydrogenation lies outside the scope of this review, but as an example of the progress which has been made with the use of special catalysts may be cited the work of J. Varga and I. Makray [23] and H. Tropsch.[24] The former investigated the high pressure hydrogenation of a gasoline containing about 50 per cent. unsaturates and 3·8 per cent. sulphur obtained by cracking of brown coal tar. With a MoO_3 catalyst under an initial pressure of 80 ks./cm.,^{2} the unsaturates were mainly transformed into aliphatic, and, to a lesser extent, aromatic and hydro-aromatic bodies. The percentage of sulphur in the reaction product decreased progressively with rising temperature. At 380° C., 36·7 per cent. of the sulphur was removed, at 400° C. 70 per cent., whilst at 440° C. only 0·4 per cent. of the sulphur remained. At 440° C. an 88·3 per cent. yield by volume of gasoline was produced, which had a very low gum test and contained only 1·5 per cent. of unsaturated compounds.

Tropsch studied the hydrogenation of phenols, using the metal catalysts covered in the I.G. patents, and found that whereas nickel is a good catalyst, its activity decreased under the influence of sulphur. Molybdenum, however, even in the form of a sulphide catalyst, seems to be an extremely active catalyst, giving a complete reduction to hydrocarbons.

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[22] See Haslam and Russell, *Ind. Eng. Chem.*, 1930, **22**, 1030.
[23] *Brenn.-Chem.*, 1931, **12**, 389.
[24] *Brenn.-Chem.*, 1930, **11**, 449.

Analytical Methods.

Although the imperfections of existing methods of identifying, separating and estimating petroleum hydrocarbons are fully acknowledged, owing to the complexity of the materials to be handled, analytical methods, perhaps with the exception of the advances made in petroleum gas analysis, can scarcely be said to be keeping pace with the progress made in other departments of the industry. For example, although cracked petrol is being used in ever-increasing quantities, the important question of gum determination has still to be set on a sound basis. Present methods of gum estimation all have their defects, and it still remains to devise a test which will give a reliable reproduction of the conditions obtaining in the engine induction system. At the present juncture the methods of the type of Hunn, Fisher and Blackwood [25] seem to give the best indication of the gum present at the time of testing, and are well suited to routine work, whilst for the estimation of " potential " gum the oxygen bomb method, due to Voorhees and Eisinger,[26] seems most satisfactory, and has been adopted by the U.S. Army and Navy in their specifications.

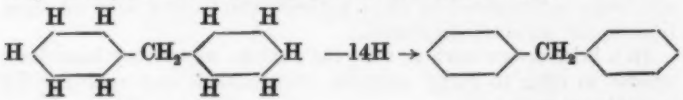
Again, it is still very difficult to predict with any semblance of accuracy the engine quality of a petrol from such purely analytical data as the bromine or iodine number, or the content of aromatics, or unsaturates determined by sulphuric acid. The chemist has yet to arrive at a method of measuring anti-knock quality that will supersede that costly and tyrannical piece of equipment—the knock testing engine.

Efforts are still being made on the subject of the estimation of aromatics and olefins by sulphuric acid. After a survey of the methods available, W. F. Faragher, J. C. Morrell and I. M. Levine [27] have recommended determination of the total olefin-aromatic content by treatment with 91 per cent. sulphuric acid, distillation to remove polymers and final treatment of the distillate with 98 per cent. acid to remove the small amount of olefins and aromatics which defied previous treatment. They have advocated the estimation of olefins alone by reaction with sulphur monochloride, distillation of the mixture at atmospheric pressure for the low boiling fractions, and subsequently at reduced pressure to remove the olefin-free oil, this to be followed by determination of aromatic hydrocarbons in the distillate of olefin-free oil by nitration. Aromatic and naphthenic hydrocarbons with olefinic side chains are included among the olefins.

[25] *Oil and Gas J.*, 20.12.28, **27** (31), 152; *J.S.A.E.*, 1929, **24**, 584; *A.P.I. Bull.*, 1929, **10** (2), 169.
[26] *Nat. Petr. News*, 23.10.29, **21** (43), 65.
[27] *Ind. Eng. Chem. Anal.*, 1930, **2**, 18.

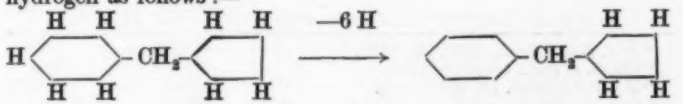
Bearing on the estimation of the olefins, W. R. Ormandy and E. C. Craven [28] have pointed out that with the exception of ethylene, the reaction products formed by the inter-action of sulphuric acid and olefins are invariably saturated hydrocarbons which separate out from the acid, or highly unsaturated compounds which remain in solution. From a new series of experiments they conclude with Howes and Nash that the olefins become more resistant to attack by sulphuric acid, with increasing molecular weight. This difference between higher and lower members of an olefin series, however, is only marked with the lower concentrations of acid—when the strength of the acid is above 90 per cent., the bromine value is reduced to very small figures. However, in order completely to destroy the capacity for absorbing bromine, 100 per cent. acid must be used, 98 per cent. being too weak.

N. D. Zelinsky and his collaborators have continued their work on dehydrogenation as a means of elucidating the constitution of petroleum hydrocarbons. Up till the present, work had been confined to fractions boiling below 150° C., but the authors have now investigated Baku distillates boiling between 170°–200° C., which they dehydrogenated in the usual way, using a platinum catalyst deposited on carbon at a temperature of 300°–310° C. (*vide* N. D. Zelinsky and B. A. Kazansky [29]). These Baku fractions contained hexahydro-aromatics which were readily dehydrogenated, but also a quantity of other saturated cyclic bodies (monocyclic polymethylenes) which were not dehydrogenated and were stable towards sulphuric acid. Elaborating this selective dehydrogenation effect, Zelinsky and Titz [30] show that pentamethylene rings are not dehydrogenated where hexamethylene rings lose hydrogen. Thus bicyclohexylmethane is oxidized to fluorene as follows :—



$(C_6H_{11})_2{=}CH_2$ $(C_6H_4)_2{=}CH_2$

whilst cyclohexyl-cyclopentylmethane loses only 6 atoms of hydrogen as follows :—



$C_6C_{11}\cdot CH_2\cdot C_5H_9$ $C_6H_5\cdot CH_2\cdot C_5H_9$

[28] *J.I.P.T.*, 1931, **17**, 185.
[29] *Ber.*, 1931, **64**, 2265.
[30] *Ber.*, 1931, **64**, 183.

In another sphere reference must also be made to the work of G. H. B. Davis and E. N. McAllister,[31] who have developed a method of estimating the relative proportions of paraffin and cyclo-paraffin hydrocarbons in Pennsylvanian lubricating oil. They arrive at the empirical formula N=0·358 mol. wt.+7·7—0·3 mol. vol., where N is the number of carbon atoms per molecule present as naphthene rings. They found the viscosity of Pennsylvanian luboil is a good indication of the proportion of molecules present in the form of ring structures or as paraffinic side chains.

On this question of the relationship between constitution and viscosity, G. Hugel [32] has determined the viscosity of a great number of hydrocarbons belonging to different groups, and concluded that where a number of compounds had the same viscosity that with the highest molecular weight has the flattest viscosity-temperature curve.

Finally, H. R. Lang and his co-workers [33] have embarked on a series of determinations of certain fundamental constants of various petroleum fractions, and their mutual inter-dependence, with a view to reducing the present number of tests which are necessary fully to define a petroleum product, to the determination of a few basic characteristics.

The specific heat of various distillates from certain crude oils has been determined by the method suggested by the late Professor Callendar for water, and the variation with temperature has been shown to be practically linear, except at low temperatures (0° C.). The presence of dissolved air, however, upsets this simple relationship. Notwithstanding its importance in plant design, there is a general lack of data as to properties such as this, also as regards expansion coefficient, refractive index, etc., which are also being investigated by these authors, and further work on these lines would certainly be repaid.

In a brief review such as this, the authors regret they have been unable to refer to many valuable contributions and apologise for possible errors.

The Chemical Engineering Laboratory,
Delft. January, 1932.

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[31] *Ind. Eng. Chem.*, 1930, **22**, 1326.
[32] *Chim. et Ind.*, 1931, 26, 1282.
[33] *J.I.P.T.*, 1930, **16**, 476 et seq.

Petroleum in the U.S.S.R.

By GEORGE A. BURRELL, D.Sc., M.Am.Chem.Soc. (Member).

PRACTICALLY all Russian petroleum comes from fields which were under exploitation when the Soviet Government confiscated them. Azneft, the biggest division of the oil trust, comprises the territory around Baku, Grozneft that around Grozny, and Maineft is that region around Maikop, at the eastern end of the Caucasian Mountains. Thus, virtually, all of the oil comes from the Caucasian region between the Caspian and Black Seas.

Maineft has a future of promise, although a disastrous oil well fire, which raged for eight months, from August to late spring of 1930, virtually paralysed all activities for a time. The author saw this well burning and also attended a trial in which the director of the region, a party man, and some of the engineers were accused of negligence in allowing the well to catch fire. Three tunnels were drilled to the casing, and by means of one of them the casing was finally pinched off.

The following data gives the oil production, refining activities and export trade of the U.S.S.R. for the first ten months of 1931, and a comparison with 1930:—

	October, 1931.	(Revised) September, 1931.	October, 1930.
Production in U.S.S.R. (in metric tons)	1,988,400	1,945,370	1,729,200

Production by Individual Oil Trusts (in thousands of metric tons).

	October, 1931.	Septem-ber, 1931.	October, 1930	10 months, 1931.	10 months, 1930.	% in 10 months, comp.1931 to 1930.
Azneft.. ..	1,141·6	1,127·9	931·1	10,954·8	8,591·5	127·4
Grozneft ..	739·4	719·4	731·4	6,665·2	5,489·5	121·5
Maineft ..	61·8	51	17·1	375·7	372·7	100·8
Embaneft ..	24·7	25·8	29	278·2	294·4	94·4
Other trusts ..	20·9	21·27	20·6	201·96	131·3	153·8
	1,988·4	1,945·37	1,729·2	18,475·86	14,879·4	124·1

Drilling Figures as accomplished by Individual Trusts (in meters).

Azneft.. ..	26,113	38,227	36,863	404,902	351,099	115·3
Grozneft ..	13,400	11,656	9,157	107,425	98,208	109·4
Maineft ..	2,728	3,043	1,091	29,038	16,864	172·2
Embaneft ..	6,034	5,088	3,700	42,308	28,807	146·9
Other trusts ..	4,475	4,750	2,543	46,671	25,665	181·8
	52,750	62,764	53,354	630,344	520,643	121·1

The above figures were (in meters).

	October, 1931.	September, 1931.	October, 1930.	10 months, 1931.	10 months, 1930.	% in 10 months, comp. 1931 to 1930.
Production drilling	26,402	38,484	37,884	405,142	363,970	111·2
Prospecting in oil fields ..	12,514	11,089	5,053	107,318	76,569	140·2
Prospecting in new fields ..	13,834	13,191	10,417	117,884	80,104	147·2
	52,750	62,764	53,354	630,344	520,643	121·1
Crude Oil Refinement (in thousands of metric tons).						
Azneft.. ..	1,029·1	950·6	789·7	9,288·2	7,344·4	126·5
Grozneft ..	736·8	744·9	682·2	6,544·8	5,333·1	122·7
Maineft ..	25·9	22·6	20·6	203·4	171·9	118·2
Oil plants ..	29·4	31	30·1	264·5	252	104·9
Sredazneft ..	3·7	1·7	4·7	37·1	23·3	159·2
	1,824·9	1,750·8	1,527·3	16,338·0	13,124·7	124·5
Production of Benzine (in thousands of metric tons).						
Azneft.. ..	56·2	51·5	36·6	474·8	369·8	128·4
The above includes:						
Cracking ..	14·8	19·2	2·1	98·6	17·1	576·6
Grozneft ..	195	193·1	137·6	1,596·9	—	—
The above includes:						
Cracking ..	36·6	32·3	1	207·8	8·9	2,300
Gas	8·1	8·3	6·5	67·6	42	161
Other trusts ..	8·2	7·7	6·8	68·1	53	128·4
	259·4	252·3	181·0	2,139·8	1,495·2	143·1
Production of Kerosine.						
Azneft.. ..	185·6	208·7	133·8	2,017·2	1,709·6	118
Grozneft ..	154·7	133	130·5	1,053·3	917·3	114·8
Other trusts ..	9·5	9	10·3	81·1	71	87·5
	349·8	350·7	274·6	3,151·6	2,697·9	116·8

Sale of Oil Products (in thousands of metric tons).

	October, 1931.			October, 1930.		
	Int. Cons.	Exports.	Total.	Int. Cons.	Exports.	Total.
Benzine and Ligroine ..	68·8	196·6	265·4	41·7	126	167·7
Kerosine ..	266·5	49·9	316·4	225·5	78·8	304·3
Diesel-fuel and gas oil ..	133·7	51·74	185·44	98	31·5	129·5
Heavy lubricating	21·5	—	21·5	27·1	—	27·1
Other lubricating	51·1	20·6	71·7	41·1	13·45	54·55
Mazut (fuel oil)	582·8	138·54	721·34	590·9	110·5	701·4
Solar oil ..	—	4·9	4·9	—	6·5	6·5
Crude oil ..	—	8·3	8·3	—	6·4	6·4
Sakhalin oil ..	—	25	25	—	—	—
Asphalt ..	—	0·4	0·4	—	—	—
Other products	—	—	—	—	0·05	0·05
	1,124·4	495·98	1,620·38	1,024·3	373·2	1,397·5

Export of Oil Products (in thousands of metric tons).

	October, 1931.	Septem-ber, 1931.	October, 1930.	10 months, 1931.	10 months, 1930.	% 1931-1930.
Kerosine ..	49·9	58·4	78·8	560·1	650·7	86·1
Benzine and ligroine ..	196·6	172·7	126	1,467·73	1,213·8	120·9
Lubricators ..	20·6	22·4	13·4	185·27	170·5	108·6
Solar oil ..	4·9	—	6·5	35·5	59·5	59·7
Gas oil.. ..	44·84	48·1	28	324·28	347·3	93·4
Diesel fuel ..	145·3	114·72	113·9	1,509·61	1,322·3	114·1
Mazut (fuel oil)	0·14	1·9	0·1	3·78	10	37·8
Crude oil ..	8·3	8·9	6·4	132·8	162·1	81·9
Sakhalin oil ..	25	32	—	107	41·5	257·8
Asphalt ..	0·4	—	—	5·9	0·1	5,900
Other oil products ..	—	—	0·05	0·14	6·84	—
	495·98	459·12	373·15	4,332·11	3,984·64	108·7

Exports by Countries (in thousands of tons).

	September, 1931.	August, 1931.	September, 1930.	3rd Qtr., 1931.	3rd Qtr., 1930.
Germany	40·1	33·2	45·3	92·7	159
England	69·7	101	87·8	249·9	234·9
France	62·7	66·2	39·6	241·5	131
Italy	75·5	93·7	82·7	244·3	214·8
Belgium	8·6	7	8·7	33·4	24
Spain	24·4	24·4	23·1	50·7	87·9
Czechoslovakia ..	19	8·2	8·4	38·7	22·4
Austria & Hungary	5·1	12·9	20	22	40·3
Denmark	23·7	9·2	1	59·9	13·1
Sweden	1·2	8·7	1·4	28·6	10·6
Turkey	2·8	14	7·7	16·8	28·1
Egypt	11	6·9	26·2	27·9	51·1
India	8·6	16·7	—	33·9	39·5
South Africa ..	31·8	10·4	4·9	52·8	27·9
Manchuria	—	0·3	—	—	0·7
Japan	32	20	—	72	—
Bulgaria	0·7	—	—	0·7	—
South America ..	—	—	3·4	5·9	11·9
Greece	—	—	7·4	—	15
China	9·5	—	—	9·8	—
Latvia & Lithuania	2·2	0·27	0·2	5·87	15·3
Finland	0·6	0·33	2·8	1·47	8·7
Esthonia	0·2	0·14	0·4	0·5	3·9
Persia	6	4·6 ..	3·9	14·7	10·6
Arabia	—	1·7	0·8	1·7	0·8
Bunker oil	22·4	20·4	12	60	39
	457·8	460·24	387·7	1,365·74	1,190·5

The foregoing data shows that the U.S.S.R. refines about 89 per cent. of the total production, and exports about 27 per cent. of these products.

Refineries at Baku comprise continuous shell stills, tube stills, cracking units and lubricating and asphalt plants. The same is true at Grozny. Maineft has no refining facilities of its own.

Azneft oil (Baku) is piped to Batoum, 535 miles away, in a 10-in. line, for refining and export, and Grozneft oil (Grozny) is piped to Tuapsi, 390 miles away, also in a 10-in. line for refining and export. Both of these towns on the Black Sea possess some refining facilities, but most of the oil is refined at Baky and Grozny.

Modern pipe stills have been built by the Foster Wheeler Corporation and the Badger Corporation, both of the U.S.A. The Badger installation at Grozny is the largest in the world, one unit reducing 25,000 barrels of crude oil per day. A number of tube stills are Russian-built.

The cracking units comprise about fourteen Winkler-Koch units, built by the Winkler-Koch Company, and six Jenkin units. Thirty more Winkler-Koch units of Russian construction are in course of erection. The octane number of Russian gasoline is low.

The lubricating department at Grozny is out of date, but a battery of modern Sharpless centrifuges is being built at Baku (Asneft) to produce 40,000 tons of lubricating oil per year.

New refinery construction is going on at Baku, Grozny, Batoum and Tuapsi, long-established refining centres, and new plants are being built, or will be built, at Krasnadar and Armirvir, in the Caucasus, to refine crude oil from Grozny and Maikop. Plants are being built at Moscow, Samara and Stalingrad to refine crude oil from Baku, *via* the Volga River.

Two refineries to refine Sakhalin crude oil will be built at Khaharovsk and Vladivostok. Sakhalin Island is off the coast of Siberia. Japan owns part of the island. A new plant will also be built at Kokand and in the Uzbekistan to refine oil from Central Asiatic fields.

The 1933 construction programme calls for the building of refineries to refine oil from Georgia, the Urals, and Kazakstan, but this construction depends upon the development of new fields discovered in those localities. A pipe-line is being built from Grozny to Armivar, both in the Caucasus, and another one is planned from Armivar to Kisky in the Central Black Sea region, if Maikop develops as anticipated. A pipe-line from Grozny to the Ukrain is already under construction. A pipe-line from the Temir oil field of the Embaneft is planned for 1933. Altogether the plan calls for laying 1750 miles of pipe-line in the next two years.

The oil fields are electrified, and all drilling is done with rotary rigs.

The writer furnished plans and specifications for Grozneft to produce about 800 tons (about 330,000 gals.) of gasoline per day. Plants include compression and absorption ones, and P.D.

stabilisers for the cracking units. Gas from the wells, from the straight refining units, from the tanks and from the cracking units will be stripped. At the completion of the present programme Grozny will have about 30,000,000 cub. ft. of gas per day from all these sources. Little progress has been made in utilising gas or producing natural gasoline in and around Baku, although plans are being pushed for these purposes.

The U.S.S.R. claims that its oil resources are of the order of 5,000,000,000 tons. The petroleum industry is adequately equipped with research facilities. The Research Institute at Grozny houses about 350 workers. Dr. A. Sakanov, a Finn, who ably headed the institution since its erection, has left Russia and is now in Finland.

World's Production of Crude Petroleum.

By GEORGE SELL (Member).

THE total world's production of crude petroleum in 1931, as far as can be estimated from the information available, was over 7,000,000 metric tons below that of 1930.

The accompanying table gives the world's production by countries for the years 1927 to 1931, those for the latter year being based upon the preliminary figures available at the beginning of 1932. From this it will be seen that the peak year was 1929, with a total production of 206,603,000 metric tons. Since then the production has steadily declined, particularly in the case of the United States of America. While the total production from all other countries has shown an increase of about 5,000,000 tons in 1931 as compared with 1929, the U.S.A. production has been reduced by over 21,000,000 tons in the same period. This is mainly due to the restrictive measures taken to counteract the overproduction of crude petroleum in the United States.

The total production from the British Empire in 1930 reached its maximum in 1930, with an increase of about 30 per cent. over the 1927 figure. In 1931 there was a slight decrease, although the percentage of the total world's production was the same as in 1930.

	1927.		1928.		1929.		1930.		1931.	
	Quantity.	Percentage of Total.	Quantity.	Percentage of Total.	Quantity.	Percentage of Total.	Quantity.	Percentage of Total.	Quantity.	Percentage of Total.
United States	123.486	70·6	123.592	67.3	138,104	66.9	123,184	62.5	116,636	61·4
Russia	10,554	6·0	11,634	6·3	14,148	6·9	18,567	9·4	22,240	11·7
Venezuela	9,384	5·4	15,710	8·6	20,402	9·9	20,308	10·3	17,648	9·3
Rumania	3,669	2·1	4,282	2·3	4,837	2·3	5,744	3·0	6,630	3·5
Persia	5,326	3·1	5,763	3·1	5,549	2·7	6,030	3·1	5,830	3·1
Mexico	9,715	5·6	7,598	4·1	6,733	3·3	5,956	3·0	4,979	2·7
Dutch East Indies ..	3,694	2·1	4,308	2·4	5,238	2·5	5,597	2·8	4,800	2·5
Colombia	2,144	1·2	2,841	1·6	2,911	1·4	2,906	1·5	2,605	1·4
Argentina	1,372	0·8	1,323	0·7	1,365	0·7	1,305	0·7	1,682	0·9
Trinidad	737	0·4	1,053	0·6	1,194	0·6	1,290	0·7	1,364	0·7
Peru	1,340	0·8	1,591	0·9	1,777	0·9	1,859	1·0	1,330	0·7
India	1,129	0·6	1,229	0·7	1,229	0·6	1,249	0·6	1,153	0·6
Poland	723	0·4	743	0·4	675	0·3	663	0·3	586	0·3
Sarawak	712	0·4	751	0·4	760	0·3	703	0·4	531	0·3
Sakhalin	69		106		168		268	0·1	332	0·2
Egypt	184		269		271		293	0·1	283	0·1
Japan and Formosa ..	248		270		281		271	0·1	276	0·1
Ecuador	76		154		196		222	0·1	250	0·1
Germany	97		92		103		169		240	
Canada	61	0·5	80	0·6	143	0·7	192		198	
Iraq	45		95		116		130		128	
France	73		74		76		75	0·3	74	0·4
Czechoslovakia.. ..	16		14		14		24		28	
Italy	6		6		6		8		20	
Bolivia	—		—		—		7		3	
Other countries ..	3		4		7		8		7	
Total	174,843	100·0	183,582	100·0	206,303	100·0	197,028	100·0	189,853	100·0
British Empire.. ..	2,639	1·5	3,133	1·7	3,226	1·5	3,434	1·7	3,246	1·7